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Chemical effects of photonuclear reactions in the propyl bromides

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CHEMICAL EFFECTS OF PHOTONUCLEAR REACTIONS
IN THE PROPYL BROMIDES

by

Albert Edward Richardson

A Dissertation Submitted to the
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INTRODUCTION

The phenomenon of chemical change as a result of recoil from nuclear reactions was first observed by Szilard and Chalmers (1) who showed that the radioactive atoms formed by neutron capture could be separated from the parent molecules and concentrated. This discovery opened up the field of research in the chemical effects of nuclear transformations, the so-called "hot-atom" chemistry.

When an atom undergoes a nuclear transformation, it must by momentum considerations acquire an energy of recoil. In many such transformations this energy is much greater than the energy by which the atom is held in chemical combination. The result is that the atom will be freed from its original molecular state. There can be little doubt that the recoiling atom will break some, perhaps many, chemical bonds as it loses its recoil energy, but the exact processes by which the recoil atom does or does not reenter into chemical combination are still far from being well understood.

The "hot-atom" chemist has, in general, made the attempt to determine the chemical forms in which the recoil atoms are finally found and how varying the conditions of temperature, phase and composition affect the relative amounts of these radioactive chemical forms. In this way he has hoped indirectly to get at the mechanisms involved.

By far the greatest number of studies in this field have been concerned with recoil atoms activated by thermal neutron capture. Several studies have been carried out with atoms activated by isomeric transition γ -rays. In this second case the recoil is usually not great enough to rupture chemical bonds, but in cases where internal conversion

occurs the atom is left in a highly ionized state and decomposition occurs as a result of the ionization. A few studies have been carried out involving atoms chemically activated by α -decay and β -decay in which case the atoms produced are non-isotopic with target atoms. Other investigations in which non-isotopic product atoms are produced have been concerned with (n,p) , (n,α) and (p,n) reactions. Recently $(n,2n)$ and (d,p) reactions have been added to the list of those producing isotopic product atoms.

Perhaps the least used method of activation has been that using high energy γ -rays. Because of the availability of the 65 Mev Iowa State College synchrotron, it was felt that a study involving photo-activated recoil atoms might be successfully carried out. A primary concern in such a study is the extent of radiation damage to the target compound in the very high x-ray fluxes involved when photoactivation is used. However, if the radiation damage were found to be of little importance the information gained from studies such as these could provide valuable comparison to the previous (n,γ) work.

Recent investigations by Fox and Libby (2), and Friedman and Libby (3) have involved the determination of the yields of the various radiobromide compounds formed during the thermal neutron irradiation of the propyl bromides. Further work along these lines has been carried out by Chien (4), and Evans and Willard (5) have very recently reported a gas phase chromatographic method of determining the relative yields of organic products which indicates that about twice as many products are produced in the propyl bromides as had previously been reported (2,4). Since 4.6 hour $\text{Br}^{80\text{m}}$ can be produced both by (γ,n) and (n,γ) reactions, the propyl bromide system seemed a logical one with which to start the

comparison of the two methods of activation. In the case of the (γ, n) reaction the initial energy of recoil would be much greater, and the importance of the initial recoil energy could be elucidated by comparing the results from the two activation methods. Such consideration as this have prompted the present investigation of the chemical effects which result from the photonuclear activation of the propyl bromides.

The historical development of the whole field of "hot-atom" chemistry provides a striking example of the interdependence of chemistry and physics. To give the reader a better appreciation of the field as it now stands a fairly complete review of the literature is presented in the next section. For further information one is referred to the excellent reviews of the field compiled by Willard (6,7) in 1953 and 1955.

REVIEW OF THE LITERATURE

Discovery and Early History of "Hot-atom" Chemistry

Not long after the discovery of the neutron E. Fermi and his coworkers (8, Amaldi and others) showed that a large number of elements are capable of capturing neutrons to form radioactive isotopes, especially if the neutrons are slowed to thermal energies. One disadvantage connected with these product radioactivities was that they were isotopic with the target, and no chemical technique by which they could be separated from the target atoms was known at the time. There was, however, an increasing demand both by physicists and by researchers in various other fields to produce these isotopes in high specific activities.

It was theorized that about 0.009 mass units would be converted into energy (about 7 to 9 Mev) in the neutron capture process. Since beta decay following such activation took care of only 2 Mev or less, it was suspected that γ -rays would be given off with maximum energies of 5 to 7 Mev. The observation that such γ -radiation accompanied neutron capture was reported by D. Lea (9), who observed γ -radiation accompanying neutron capture by hydrogen to form deuterium.

Soon after Lea's discovery, Szilard and Chalmers (1) performed their very important experiment. They irradiated ethyl iodide containing a trace of iodine with neutrons from a Rn-Be source. Following the irradiation they shook the ethyl iodide with an aqueous reducing solution and precipitated silver iodide. By this method they were able to increase the counting rate by a factor of ten. Such an increased specific activity could only be explained on the basis that bond rupture had occurred as

a result of recoil from the nuclear reaction.

For γ -rays of the energies predicted the recoil energy would be about 100 ev for an I^{128} atom. Since the carbon-iodine bond has an energy of only about 2 ev there was little doubt that this recoil could cause bond rupture. Several early workers (10,11,12) reported energies of capture γ -rays ranging up to about 7 Mev which gave further proof that bond rupture must have occurred.

The Szilard-Chalmers technique was immediately given widespread use in producing high specific activity samples of (n, γ) induced activities. Erbacher and Philipp (13) and Suë (14,15) reported minimum enrichment factors of 2.4×10^6 and 2.3×10^6 , respectively, for Szilard-Chalmers techniques in which irradiated organic halides were extracted without resorting to isotopic carriers.

The literature contains many reports of investigations in which the Szilard-Chalmers method has been applied to produce high specific activity for various types of problems involving tracers (16,17,18,19, 20,21,22,23,24,25,26). The Szilard-Chalmers technique can be used to increase the specific activity only if the rate of thermal exchange between the parent compound and the recoil atoms is quite slow.

There have been some reports that bond rupture may not have occurred in the pile irradiation of cystine (27) and vitamin B₁₂ (28). If such were the case vitamin B₁₂, for instance, could be tagged directly with Co⁶⁰ without going through a complicated synthesis. However, more recent workers (29,30) have found no evidence for such tagging in the case of vitamin B₁₂.

A recent study made by Boyd, Cobble and Wexler (31) involved the application of the Szilard-Chalmers technique to pile irradiated KBrO₃.

They reported a 22,000 fold enrichment of 35.9 hour Br^{82} , but they also found that the specific activity decreased with time and was independent of the intensity of the source. This indicated that radiation decomposition was not important, but that the free radicals were recombining, possibly with the help of the radiation.

In the case of compounds less stable than KBrO_3 the amount of radiation decomposition could be very important. If, for instance, an appreciable fraction of inactive atoms were released by radiation damage, they would greatly diminish the specific activity of the active atoms released by γ -recoil,

The fact that not all of the radioactive atoms could be removed from organic target compounds by the Szilard-Chalmers technique prompted early workers to investigate the chemical nature of the compounds in which the radioactive atoms were "retained". The methods applied involved the addition of macroscopic amounts of the compounds expected. The radioactive molecules would be carried in the various compounds. These could then be separated and counted to determine the relative yields of the various suspected radioactive forms which were produced in the retention process.

Gluckauf and Fay (32) carried out the first detailed investigation of the chemical effects of radiative neutron capture. These workers selected the alkyl halides for their studies because it was known that halogen atoms exchanged very slowly with alkyl halide molecules. They were able to show that active iodine and bromine atoms could substitute for either hydrogen or halogen atoms in the process of losing their recoil energies. Thus, although thermal exchange was not taking place it definitely appeared that exchange with high energy or "hot" atoms

was taking place.

The main bulk of the work in "hot-atom" chemistry has involved the study of the chemical effects resulting from radiative neutron capture much like the pioneer work of Gluckauf and Fay; and alkyl halide systems have received the most study because of their relatively simple chemical properties and the favorable nuclear properties of the halogens.

Chemical Effects of Activation by Isomeric Transitions

The isomeric transition method of activation provides a very clear example of the interdependence of physics and chemistry. Segré, Halford, and Seaborg (33) and, independently, Devault and Libby (34) showed that 18 min Br^{80} is the isomeric daughter of 4.6 hr Br^{80m} . Each used the Szilard-Chalmers technique of extracting the Br^{80} atoms away from the parent compound. In the case of the Br^{80m} transition the recoil energy expected from the 43 Kev γ -rays (35,36) is only about 0.02 ev. If the γ -ray were converted in the K-shell the recoil energy would still be only about 0.2 ev. Since most bond energies fall in the range from 2 to 5 ev it is apparent that recoil would not be sufficient to cause bond rupture.

It was finally shown very definitively by Seaborg, Friedlander, and Kennedy (37) that bond rupture requires internal conversion of the low energy transition γ 's. They prepared gaseous tellurium diethyl containing Te^{127} and Te^{129} and zinc diethyl containing Zn^{69} . It was found that no bond rupture occurred in the case of the zinc diethyl even though the transition γ -ray for Zn^{69} had an energy of 0.47 Mev. However, a definite amount of tellurium activity was separated from the tellurium diethyl as a result of the transition γ 's of Te^{127} and Te^{129} . The energies

of these γ 's were known to be about 0.1 Mev or about one-fifth the energy of the Zn^{69} transition γ -ray. Gamma recoil could therefore not explain the bond rupture in the tellurium diethyl. It was known, however, that the γ 's in tellurium were largely converted whereas those in zinc were not. These authors thus predicted that the high state of electronic excitation that results from the loss of a conversion electron is responsible for the accompanying isomer separation process due to the operation of the Franck-Condon principle. Not long after the above work was carried out Cooper (38) showed theoretically that internal conversion or K-capture can cause bond rupture by means of Auger processes (39). In these processes the vacancy in a low lying shell results in readjustment of several electrons to fill the vacancy. In a recent investigation Wexler and Davies (40) have shown that the average charge resulting from the $\text{Br}^{80m} \rightarrow \text{Br}^{80}$ transition is plus ten. Miskel and Perlman (41) have shown that the average charge on Cl^{37} formed by electron capture in A^{37} is about plus 4.

The importance of discussing the chemical effects resulting from isomeric transition, in which recoil energy plays little part in bond rupture, may not be evident at first. It is apparent that the only energy which the highly charged Br^{80} atom will have following the γ -transition will be that resulting from the repulsion of positive nuclei and the attraction of planetary electrons. It must therefore depend mainly on electronic excitation to get back into chemical combination. One might expect ionic reaction mechanisms. On the other hand in the case of recoil from thermal neutron capture γ -rays the energy of the freed atom is great enough to cause fragmentation in the medium. If the medium were essentially one which involved covalent bonds, the highest probability is that such

fragments would be free radicals. In the (n,γ) case one would expect that any charge the recoil atom might acquire as a result of the γ -emission would most likely be neutralized long before the atom had become "thermalized", that is, in thermodynamic equilibrium with the surrounding medium. This would be expected because of the many collisions required to lower its energy to a thermal one. Thus in the case of (n,γ) reactions one might expect predominantly free radical type mechanisms, and, if so, chemical effects resulting from the (n,γ) processes would most likely be quite different from those resulting from isomeric transitions.

Apparently bond rupture does not always occur as a result of the $\text{Br}^{80\text{m}} \rightarrow \text{Br}^{80}$ transition. Experiments with bromine compounds which were designed to prevent re-entry of a freed atom back into the parent molecule have shown that anywhere from 0 to 100% of the bromine may be retained (42,43,44). Thus, there is definite evidence that even with an average plus charge of 10 in a Br^{80} atom, bond rupture may not take place.

Magee and Gurnee (45) have indicated among other things that the lowest electronic states of simple HBr^{+x} molecules may be homopolar states which are stable with respect to dissociation into H^+ and $\text{Br}^{+(x-1)}$. This is somewhat borne out in the data of Hamill and Young (42) in which gaseous HBr shows an apparent failure of bond rupture 25% of the time and DBr , 16% of the time.

Most comparative studies have shown that (n,γ) activation and isomeric transition lead to somewhat different chemical effects. This might have been expected on the basis of the preceding discussion. However, there has been some experimental evidence to the effect that some of the γ 's given off in (n,γ) reactions are of low enough energy to be similar to isomeric transition γ 's and are emitted quite long after the initial bond

rupturing γ 's. These delayed γ 's could give rise to chemical effects similar to those of the $\text{Br}^{80\text{m}} \rightarrow \text{Br}^{80}$ isomeric transition.

Hibdon and Muehlhaue (46) have observed the conversion electrons from neutron capture in $^{113}_{48}\text{Cd}$, $^{149}_{62}\text{Sm}$, $^{149}_{64}\text{Gd}^{\text{odd}}$, $^{164}_{66}\text{Dy}$, $^{199}_{80}\text{Hg}$ with a 180° γ -ray spectrograph. The expected lifetimes of the transitions are in the range of from 10^{-12} to 10^{-9} seconds. Also, other recent data have shown evidence of a positive charge on the recoil atoms resulting from (n, γ) activation. Wexler and Davies (47) have reported that at least 12% of $\text{Br}^{80\text{m}}$, 25% of Br^{82} , 50% of I^{128} , and about 18% of Br^{80} is positively charged during stabilization of the product nucleus following neutron capture. Yosim and Davies (48) have shown that the majority of the gold and indium atoms which recoil from thin films of gold and indium during neutron irradiation are positively charged. This charge must be produced by some kind of an internal conversion process which must occur long enough after the emission of the initial energetic γ -rays to allow the atoms to leave the surface, or their charge would be neutralized before they escaped.

Hornig, Levey and Willard (49) have shown that in about 45% of the neutron capture events in the $\text{I}^{127}(n, \gamma)\text{I}^{128}$ reaction $\text{CH}_3\text{I}^{128}$ is produced when a mixture of I_2 and CH_4 is irradiated. In the same experiment I^{131} was introduced as molecular iodine, and I^{131} atoms were produced photochemically. Production of $\text{CH}_3\text{I}^{131}$ was not observed indicating that the mechanism did not involve free radicals. These workers postulated that the reaction must occur in an inversion type step between a hot I^{128} atom and a methane molecule. They suggested that the reaction occurs as a result of internal conversion of part of the energy of the (n, γ) process rather than completely as a result of the kinetic energy.

The system which has given the widest variation of results for the two methods of activation is that of a mixture of bromine and toluene. The ratio of toluene bromide to benzyl bromide as determined by Gavoret and Ivanoff (50) was 0.12 by isomeric transition and 0.8 by neutron capture. The ortho/meta/para ratio in both cases was 4/2/1.

Bohlman and Willard (26,51) have made a comparison using a mixture of bromine and tetrachloroethylene. They found organic yields of 37% in the liquid solution and 0% in the gas phase for the (n,γ) process, in contrast to 85% and 19%, respectively, for the isomeric transition process. The double bond seems to exhibit a much greater affinity for the isomeric transition activated Br^{80} than for the (n,γ) activated Br^{80} . Similar results on a less marked scale have been observed in the systems $\text{Br}_2\text{-CCl}_4$ (51,52) and $\text{Br}_2\text{-CCl}_3\text{Br}$ (53). In the $\text{Br}_2\text{-CCl}_4$ liquid solution the total organic yields depended upon the mode of activation. However, the yields of $\text{CCl}_3\text{Br}^{80}$, $\text{CCl}_2\text{BrBr}^{80}$ and higher boiling products were, within the experimental error, in the same ratio regardless of the mode of activation. One thus suspects that the chemical yields were dependent on the relative probabilities for the occurrence of the various types of collisions necessary to produce the given products.

Very recently Levey and Willard (54) have carried out an investigation of the yields of organic products resulting from the $\text{Br}^{80\text{m}}(\text{I.T.}) \text{Br}^{80}$ reaction in the propyl bromides. The relative yields are found to be strikingly similar to the results previously determined for the $\text{Br}^{79}(n,\gamma) \text{Br}^{80\text{m}}$ reaction in the propyl bromides (2,4).

Some questions come to mind as concerns the comparison of these two methods. How might the results from the (γ,n) mode of activation be expected to compare with those from the above two methods? How would the much greater

recoil energy enter in, and would there again be the possibility of γ 's being given off as the compound nucleus stabilizes itself into the radioactive product? Perhaps experimental results on the chemical effects of the (γ, n) process will help to answer these questions.

Chemical Effects of Activation by Radiative Neutron Capture

Gas Phase Investigations

Studies of the chemical effects resulting from the (n, γ) process in gaseous systems have been fruitful in explaining various aspects of "hot-atom" chemistry.

Dancoff and Kubitschek (55) have recently reported that the total energy of γ -rays emitted in the radiative neutron capture process is 5 to 10 Mev. Using the momentum equation,

$$E_M = 536E_\gamma^2/M \text{ ev,}$$

where E_γ is the γ -ray energy in Mev and M is the mass of the recoiling atom in amu, one can determine the recoil energy of that atom. If one assumes that a single γ -ray is given off and that the atom has a mass of 100, then the recoil energy will be about 150 ev. Since chemical bond energies range from 2 to 5 ev there is little doubt that bond rupture would take place in such a case. However, in general, two to six γ -rays are given off (56). There is the possibility that these are given off simultaneously and with such angular relation that the momenta would cancel giving very little recoil energy to the activated atom. This is a small fraction as shown by Cobble and Boyd (57) who calculated that the portion of atoms from the $\text{Br}^{81}(n, \gamma)\text{Br}^{82}$ reaction which receive less than 10 ev recoil energy is about 5, 3 and 1.5% for the emission of 6, 4 and 3 γ -rays, respectively. As was

brought out earlier there is indication that some of the γ -rays are given off much later than the initial one in which case they would not be simultaneous and the momenta would not cancel. Molecular vibrations have periods of the order of 10^{-14} seconds and if the elapsed time between the emission of γ 's is longer than this, the γ 's will not act as if simultaneous as far as bond rupture is concerned.

Suess (58) has indicated that if the molecule containing the activated atom is not dissociated immediately the whole molecule may recoil. In such a situation the internal energy, E_1 , available for bond rupture, is the difference between the recoil energy of the activated atom and that of the whole molecule,

$$E_1 = E_m(M' / [M' + M])$$

where M is the mass of the activated atom and M' is the mass of the rest of the molecule. Perhaps this explains why Williams and Hamill (42,59) have found that some 25% of the Br^{80} atoms resulting from the $\text{Br}^{79}(n,\gamma)$ Br^{80} process in a mixture of HBr and a trace of α,β -dibromoethylene remain in inorganic combination. Since these workers had pretty well established that all thermalized bromine atoms would enter organic combination only by exchange with the olefin, the only possibility other than nonrupture of the bond would be that an exchange reaction involving "hot" atoms occurs. These same workers (59) have shown that about 13% of the bromine atoms activated by the $\text{Br}^{79}(n,\gamma)$ Br^{80} process in ethyl bromide at 700 mm pressure form HBr by a "hot" reaction ($\text{Br} + \text{RH} \rightarrow \text{R} + \text{HBr}$) before they have been thermalized. Hamill and Young (42) believe that this same type of reaction occurs to a certain extent in the case of activation by isomeric transition in gaseous $\text{CH}_3\text{Br}^{80\text{m}}$. There is also evidence that 1 to 3% of the recoil halogen atoms from the neutron irradiation of gaseous ethyl bromide (59)

and gaseous ethyl iodide (59) may reenter organic combination by "hot" processes. Other studies (60,61,62,63,64,65) in photochemistry and radiation chemistry have indicated that "hot atom" and "hot radical" reactions may be important.

Apparently such considerations as momentum cancellation and energy available for bond rupture are seldom of importance in gas phase reactions induced by neutrons, since almost complete bond rupture has been noted in nearly all investigations. Wexler and Davies (47) have reported 1% retention of $\text{Br}^{80\text{m}}$ in ethyl bromide, Libby (66) had previously reported 5% in the same system at high gas pressures, and Suss (58) had reported 3% from measurements on the Br^{80} isomer. Other cases which leave little doubt that the (n,γ) process is nearly 100% efficient in producing bond rupture are the 2% retention of Cl^{38} activity from the (n,γ) reaction on butyl chloride (67) and the less than 1% retention of Br^{82} in CF_3Br (68). One would expect that if bond rupture occurs in the gas phase it would also occur in condensed phases.

Rice and Willard (68) have noted that the organic yield in CF_3Br increased as a function of gas density. They felt that this might be explained by assuming that the diffusion coefficients of the organic radicals formed around the recoil atom are decreased more by the density increase than are the diffusion coefficients of the inorganic fragments. Such a consideration will be discussed later in connection with organic yields in condensed phases.

Investigations Involving Oxy-anions of Inorganic Salts

A few studies have been carried out on the chemical effects of the (n,γ) reaction which occur in inorganic salts containing oxy-anions.

No distinct comparison with the effects produced in the alkyl halides can be made because of the different chemical nature of these two types of substances. The chemical effects which have been noted in the inorganic studies seem to indicate that a range of recoil energies exists for a given (n,γ) transition. Thus, 9% of KBrO_3 irradiated in a pile appears to exhibit no bond rupture (31).

Cleary, Hamill and Williams (69) have found 20% retention as IO_3^- from neutron irradiated solutions of NaIO_3 over a wide range of concentration and pH. However, the yield was reduced to 6%, but no lower, by the addition of I^- or CH_3OH and raised to 40%, but no higher, by the presence of IO_4^- . These results indicate that in 6% of the cases no bond rupture takes place; in 34% of the cases an unstable intermediate IO_2^- is formed which is affected by the presence of oxidizing and reducing agents; and in the remaining 60% of the cases IO^- and I^- are formed which are not affected by the presence of IO_4^- . The fact that a varying number of I-O bonds are ruptured is indicative of either a distribution in recoil energies or in the probability of decomposition of a highly excited IO_4^- ion into various lower oxidation states.

It will be evident later that a similarity exists between the results of these oxy-anion studies and the results where alkyl halides are involved, at least in a general sense. Some chemical effects can be varied by the presence of additives during irradiation while others cannot. In the case of the alkyl halides certain additives which exhibit very marked effects on the ratio of organic yield to inorganic yield have come to be known as "scavengers". These "scavengers" have been quite important in showing that thermal reactions as well as "hot" reactions occur in alkyl halides activated by neutron capture.

For further reference to the literature concerned with inorganic studies involving activation by neutron capture one should refer to the reviews by Willard (6,7) and to the book by Wahl and Bonner (70).

Chemical Effects in Liquid and Solid Alkyl Halide Systems

It has been clearly shown that (n,γ) activation nearly always results in bond rupture in gaseous alkyl halides (47,49,58,59,67,68). One must, therefore, infer that the organic yields of 20% and greater which occur for these compounds in the liquid and solid phases are the result of recombination of the freed recoil atoms with the medium. In the early studies several groups of investigators (32,51,71,72,73) suggested the possibility of a Frank-Rabinowitsch "cage" (74) consisting of parent molecules and one or more radicals in which recombination would take place. The "cage" would in some cases trap the recoil atom within its walls. Once trapped the atom would enter into chemical combination with one of the radicals or with an excited molecule. Libby (75) expanded this "reaction cage" idea in terms of the energies required to break chemical bonds and to break through the "cage" wall.

Libby (75) postulated that the high initial recoil energy would remove an activated halogen atom from the vicinity of the molecular fragment from which it has recoiled. The chances of it recombining with this fragment would, of course, be extremely small. As the recoil atom passed through the surrounding medium it would lose its energy by collisions. At the initial high energies collisions even in condensed phases could be considered to be essentially elastic. (An analogy to this supposed phenomenon would be a golf ball striking a second golf ball which was enmeshed in a spider web. The web would have little effect on the momentum transfer.)

On the elastic basis the only way in which a high energy atom could lose nearly all of its excess energy in one collision would be to collide head-on with an atom of similar mass. If it collided with carbon and hydrogen atoms it would lose only a small fraction of its energy in each collision, and would retain enough energy to escape from the vicinity of radicals produced in the collision. However, if it collided with a halogen atom, there would be a definite probability that it would not have enough energy to escape from the vicinity of the radicals formed. Thus, if ϵ is considered to be the energy necessary to escape from the "reaction cage" and ν is the energy of the chemical bond holding the struck halogen atom to its molecule, it follows that the proportion of atoms which will be retained is $\frac{\epsilon}{\nu}$.

Miller, Gryder, and Dodson (76) have developed a theoretical treatment which shows that in the case in which such elastic collisions with like atoms occur, the retention (or organic yield) will be given by the equation: $R = \frac{\epsilon}{\nu}$. However, Miller and Dodson (77) showed that while the theory holds for CCl_4 and $\text{CCl}_4\text{-SiCl}_4$ mixtures in which collisions with like atoms only can occur, it breaks down in $\text{CCl}_4\text{-C}_6\text{H}_{12}$ mixtures in which collisions with carbon and hydrogen atoms are possible.

In general it has been observed that the parent molecules are predominantly formed in the recombination process even if collisions with carbon and hydrogen atoms are possible. The explanation given by Libby (75) was that, no matter what the energy of the recoil atom, if it collides head-on with a like atom, it can be captured; and retention reactions can occur for such collisions over the whole range of energies from E , the initial energy, down to, ν , the bond energy. Thus, the chance that a collision would occur with a like atom somewhere in this wide energy region with resultant recombination is probably quite high. On the other

hand, the only energy region in which the recoil atom can collide with carbon and hydrogen atoms and then lose enough energy to be retained would be the relatively narrow energy region just above thermal energies. And the main probability would be that a direct collision with a like atom would take place before the atom ever got down into this "epithermal" region.

Friedman and Libby (3) and Fox and Libby (2) carried out (n,γ) activation studies with the propyl bromides in which they attempted to determine the various organic radiobromide products formed. The results of Friedman and Libby (3) have been shown to be largely in error by the follow up investigation of Fox and Libby (2). Comparison of liquid and solid state reactions in the former investigation brought out the fact that the yields of compounds resulting from substitution for carbon and hydrogen atoms were greatly increased in solid state irradiations, whereas those which involved the replacement of bromine atoms showed little difference between solid and liquid state irradiations.

Friedman and Libby (3) suggested that the formation of dibromocompounds, the result of substituting a hot bromine for a hydrogen or carbon atom, might be explained by assuming that when the energy of the recoil atom was reduced to the order of 10 ev, a new type of energy transfer would become possible. In this energy region the halogen atom might transfer energy to molecules as a whole in inelastic collisions. Such collisions would result in molecular excitation followed by decomposition. The resultant organic radical could then combine with the halogen atom. As was mentioned earlier, there has recently been evidence for "hot-atom" reactions in photochemistry and radiation chemistry (60,61,62,63,64,65). Of course the possibility exists also that the recoil halogen atom might combine with a

hydrogen atom or a halogen atom in such collisions. Miller and Dodson (77) suggested a reaction of the type: $\text{Cl}\cdot + \text{RH} \rightarrow \text{HCl} + \text{R}\cdot$. Recent evidence strongly supports this type of reaction and will be discussed later in connection with the so-called "scavengers".

Fox and Libby (2) further verified the increased yields of dibromopropanes for the irradiation of propyl bromide in the solid state. They explained such an increase of "epithermal" products by postulating the production of a molten volume in the solid. Calculations were given to show that a highly energetic recoil atom could melt a portion of the solid involving about 1000 molecules. It was then suggested that bromine-bromine collisions leading to reproduction of the parent propyl bromide would be expected to occur mainly in the center of this pseudo-liquid volume. It was felt that little increase of yield of the parent compound in the solid state would be expected because the medium would be essentially the same as in the case of irradiation in the liquid state. However, it was felt that in the case of the "epithermal reactions" the diameter of the molten volume around the site of such an "epithermal" collision would be much smaller. In other words these reactions would take place near the edge of the molten volume, in what Libby and Fox considered to be a semi-molten region. The strength of the so-called "cage wall" would be much greater in such a liquid-solid region than in a solely liquid medium, and for this reason these workers were of the opinion that epithermal type reactions should be greatly enhanced in the solid state irradiations. One must admit that this hypothesis, at least on the surface, appears to explain the results.

One thing that was overlooked by these workers was the possibility that this pseudo-liquid volume in the solid could contain a much higher density of radicals than the irradiated liquid. In the solid the propyl bromide molecules would be expected to intertwine to a certain extent, and the process of recoil-produced melting could be accompanied by much fragmentation which would probably be greater for the solid than for the liquid. In such a case the molten volume could not be considered as exhibiting the same chemical characteristics as the ordinary liquid.

Perhaps the greatest weakness in the postulates of Fox and Libby, however, was their complete lack of consideration of the possibility of thermal type reactions. Their whole "billiard ball collision-epithermal collision" hypothesis is based solely on recombinations involving "hot" bromine atoms.

As early as 1939 Suess (58) had shown that organic yields could be increased if acetylene were added to ethyl bromide during irradiation. It was felt that the acetylene would add thermal bromine atoms easily, whereas the ethyl bromide could not. In 1950 Williams, Hamill, Schwarz and Burrell (78,79) discovered that α,β -dibromoethylene will react readily with bromine atoms, but not with bromine molecules. They also reported results which indicated that very small amounts of allyl bromide mixed with ethyl bromide could quite markedly increase the organic yield. The results seemed to indicate that thermal bromine atoms which might otherwise eventually enter into inorganic combination were being scavenged by the allyl bromide.

Similar studies by Willard and coworkers (52,53,80,81) have shown that the presence of about 1 mole per cent or less of elemental bromine in alkyl bromides or elemental iodine in alkyl iodides can reduce the organic yield

by 15%, but a further increase in the halogen concentration reduces the yield very little. They have, thus, postulated that the part of the organic yield which is relatively insensitive to added halogen can be attributed to "hot" processes. The part of the organic yield which is sensitive to added halogen can be attributed to reactions of thermalized recoil atoms with radicals which they have produced in losing their energy.

These same workers (81) have shown that the addition of 1 mole per cent of α,β -dibromoethylene to ethyl bromide increases the organic yield from 32% to 60%. Further additions show little effect. This indicates that 40% of the inorganic products are produced by "hot" processes and 28% by thermal processes. Most attempts to determine the nature of the inorganic products have not been successful. However, Chien and Willard (67) have made use of the fact that carefully purified pentene-2 will react instantaneously with tracer amounts of radiochlorine but only very slowly with hydrogen chloride. Using this method these workers have found that of the chlorine atoms activated by the (n,γ) process in butyl chloride, about 21% enter organic combination, 8% form Cl_2 and 71% form HCl . The ratio of the inorganic products is roughly the same as the ratio of the number of available hydrogen atoms to the number of available chlorine atoms in n-butyl chloride.

Recently Roy, Williams, and Hamill (82) have shown that a diffusion kinetics treatment can be applied to the atom-radical recombination process following (n,γ) activation of liquid alkyl halides. They postulated that each nuclear process produces "effectively" one atom-radical pair and that decreased recombination due to added halogen results from competition with diffusion controlled recombination. The increased organic yields caused by

added α,β -dibromoethylene were explained by the competing reactions $C_2H_5Br + Br^* \rightarrow C_2H_4Br + HBr^*$ and $C_2H_2Br_2 + Br^* \rightarrow C_2H_2BrBr^* + Br$. They found the "scavenger" reaction to have an activation energy about 11 kcal per mole smaller than that of the solvent reaction.

The question arises: How might these thermal processes be rationalized by the Libby type hypothesis?

Willard (6) has felt that the Libby hypothesis is a gross oversimplification of the recombination mechanism. He has been of the opinion that although such a hypothesis may rationalize the data for certain systems, it certainly cannot be applied to all systems as a general explanation.

He has felt that the assumption of elastic collisions in condensed phases is not justified. The work of Miller and Dodson (77), however, tends to give definite credence to such elastic collision mechanisms where collisions can occur only with like atoms in systems such as CCl_4 and CCl_4-SiCl_4 .

Willard also has been of the opinion that the indications of thermal type recombinations which were overlooked in the Libby theory lessen its credibility. There is no question that this is a definite weakness in the Libby hypothesis, but this in itself does not prove that the hypothesis is incorrect as far as it goes.

The fact that inorganic products are produced in "hot" reactions as well as thermal reactions has not, according to Willard been considered in the Libby theory. This may tend to discredit the initial $R = \frac{\epsilon}{\rho}$ hypothesis of Libby, since an atom trapped in a cage could very well react with a hydrogen atom or another bromine atom, instead of an organic radical. However, it does not prove that the Libby type recombinations do not exist.

Perhaps the best evidence against the Libby theory to date is the fact that C_2H_5I , $i-C_4H_9I$ and $s-C_4H_9I$ showed little or no change in organic yield with change in phase (80). These results alone would seem to discredit the theory as a general one. They seem to suggest the "random fragmentation" type of hypothesis which Willard has proposed. Willard (6) has been of the opinion that elastic collision mechanisms similar to those expected in the gas phase cannot be expected in condensed phases. His feeling has been that there will be much bond breaking following the initial collision of the struck atom with the condensed medium. Then when the energy of the atom has been reduced below bond-breaking energies it will find itself in, or adjacent to a pocket of high local concentration of organic radicals and inorganic atoms. If it is in a pocket of radicals it will recombine before it has had a chance to diffuse in thermal equilibrium with the system. Such a reaction would be considered a "high-energy" process since it could not be greatly affected by the addition of small amounts of scavengers. However, if it were not in a pocket of radicals, it would then diffuse as a thermal atom until it came in contact with a radical which it had directly or indirectly produced by the process of fragmentation.

The Willard theory is in essence not much different than the Libby theory. Such a hypothesis based on radical densities does not in itself deny the existence of something approaching elastic collisions in the reproduction of the parent compound. A combination of the two theories seems to provide the best answer.

One important aspect of the thermal recombination theory is that it seems to explain the effects of impurities which have in many cases resulted in high organic yields for short periods of irradiation. It was found (2)

that treatment of propyl bromides with ozone followed by careful distillation could reduce the organic yield from 50% to 35%. It was immediately apparent that olefin concentrations in the range of 10^{-7} to 10^{-4} mole fraction had been causing high organic yields. The discovery of the thermal recombination process clearly indicates why these impurities could result in high organic yields. As the thermalized atom diffused out into the system it might meet and combine with an olefin molecule before it had a chance to combine with a hydrogen or bromine atom.

Another possible explanation involves exchange of radioactive HBr or Br_2 with the olefin impurities. This latter explanation would seem to hold for the observation of Friedman and Libby (3) that organic yields would increase markedly if the irradiated samples were allowed to stand for periods up to 24 hours before the inorganic activity was extracted. Such an increase was not noted by Fox and Libby (2) when ozone treatment had been applied to remove olefinic impurities.

Another aspect of the effects of impurities concerns radiation damage resulting from high fluxes of γ -rays. It had long been inferred that the small γ -fluxes connected with neutron sources could not result in enough radiation damage to alkyl halides to affect the observed chemical effects. Fox and Libby (2) suggested that for the total γ -radiation of 700 roentgens involved for a one hour irradiation, the steady state concentration of radicals produced as a result of radiation damage would be about 10^{-13} mole fraction, which would be far below the amount necessary to produce a noticeable effect. These workers reported that the presence of about 10^{-4} mole fraction of bromine would be expected to eliminate radiation damage effects. They also showed that such concentrations of bromine could eliminate the effect of minute amounts of olefin impurities. The criterion which was

used for purity of the propyl bromide was that the propyl bromide gave the same organic yield in the pure state as it did when it contained 10^{-4} mole fraction of Br_2 during irradiation.

One of the main concerns in initiating the photonuclear study has been with the amount of radiation damage which would result for the high γ -ray fluxes involved. However, if one assumes an intensity of 3×10^4 roentgens per hour for an irradiation with high energy γ -rays, it appears that the steady state concentration of radicals produced by radiation damage will be only about 10^{-10} mole fraction unless chains are initiated. Such a concentration should exhibit a negligible effect.

Very recently Chien and Willard (83) have reported that the organic yields of pure degassed liquid n-propyl bromide can be markedly increased when the n-propyl bromide is subjected to a total γ -radiation of 10^3 roentgens or higher either before or during irradiation. The results for long irradiations in which the γ -ray flux arises from the neutron source are summarized as follows. (1) The organic yields of Br^{80} , Br^{80m} , and Br^{82} are essentially equal to each other for irradiation times up to 4 hours (6×10^3 roentgens) either in the presence or absence of air. (2) For irradiations of longer than 16 hours in the absence of air the organic yields of Br^{82} and Br^{80m} increase up to 90% and 73%, respectively for a 132 hour irradiation. (3) The organic yield of Br^{80m} does not seem to be noticeably affected by the long irradiations if the irradiation is carried out in the presence of air. The yield of Br^{82} in such irradiations does, however, increase from 34% to 48% for a 132 hour irradiation. (4) The yield of Br^{80} in the irradiation of the degassed propyl bromide decreases from 34% to 29% as the irradiation time is increased.

The reason for the decrease in the organic yield for Br^{80} is that the Br^{80} is arising from two sources: (1) directly by $\text{Br}^{79}(\text{n},\gamma)\text{Br}^{80}$, and (2) indirectly by means of $\text{Br}^{80\text{m}}(\gamma)\text{Br}^{80}$. The organic yield for the latter transition is 20%. The directly formed Br^{80} will attain equilibrium with the neutron source very soon after the start of the irradiation. As the irradiation progresses the amount of $\text{Br}^{80\text{m}}$ will also increase until secular equilibrium with the neutron source is reached. Since the Br^{80} is in equilibrium with the $\text{Br}^{80\text{m}}$ almost from the start of the irradiation, as soon as saturation with respect to $\text{Br}^{80\text{m}}$ is reached the ratio of the rates of production of Br^{80} from the two aforementioned sources will stay the same, and the organic yield will decrease no further.

By subjecting the n-propyl bromide to about 4×10^6 roentgens from a 40 curie Co^{60} source and then chemically treating it prior to neutron irradiation Chien and Willard were able to eliminate the effects of the products which resulted from radiation damage. Since both ozone treatment and treatment with bromine for 12 hours eliminated the effects of the product impurities, it was surmised that the products were of an olefinic nature. Because of the much greater amount of γ -radiation which was involved when the Co^{60} source was used the organic yield of Br^{80} was increased to as high as 46%.

These results appear to uphold the suggestion of Rowland and Libby (84) concerning the isomer effects noted by Capron and Crevecoeur (85,86) with liquid organic bromides. The latter authors noted higher organic yields for $\text{Br}^{80\text{m}}$ than for Br^{80} contrary to the results of other workers (2,84). It has been pointed out that since Capron and Crevecoeur did not purify their materials, impurities may have been present in the irradiated bromide which could react with inorganic bromine to return it to organic combination.

The effect would be to increase the apparent retention of the 4.6 hour species more than the 18 minute species because of its longer lifetime. It explains why Chien and Willard have noted such a difference in the amount of increase in the organic yields of the 18 minute, 4.6 hour and 35.9 hour bromine activities when impurities are produced as a result of radiation damage.

In the studies of possible isomer effects in liquid normal and isopropyl bromides Capron and Crevecoeur (86) used pure water as their extracting solution because they feared that a reducing medium would interfere with secondary effects resulting from possible internal conversion mechanisms. This fear does not seem justified since such secondary effects, if they existed, could not be evaluated by pure water extraction anyway. No report in the literature has yet indicated an isomeric state above Br^{80m} or one other than Br^{80m} above Br^{80} that has a lifetime even of the order of seconds. Thus any internal conversion mechanisms take place at most within seconds after the initial recoil process. All studies which have been concerned with charge mechanisms seem to indicate that any charged atoms in the medium are immediately neutralized, so that any secondary effects would almost certainly occur prior to any extraction process.

There has been definite evidence for incomplete extraction of inorganic bromine when pure water is used as the extracting medium. In 1939 Lu and Sugden (71) had reported that pure water extracted about 10% less of the total activity from $\text{C}_6\text{H}_5\text{Br}$ and $\text{C}_2\text{H}_4\text{Br}_2$ than did a reducing solution such as sodium thiosulfate. They at the time felt this was due the non-extraction of bromine atoms into the water. In 1941 Devault and Libby (73) stated that Br atoms have a long life because they are not very soluble in water or conc. H_2SO_4 and don't act with such compounds as ethyl bromide.

In the course of the photonuclear studies of this thesis it has been noted that when noticeable amounts of molecular bromine were present in the irradiated propyl bromide it was sometimes necessary to add excess sodium sulfite to reduce the bromine coloration in the propyl bromide. In such cases the bromine color in the aqueous layer prior to reduction was much less pronounced than in the organic layer.

Any isotope effect that Capron and Crevecoeur (86) have reported is most likely due either to the impurities present or to a difference in the relative yields of HBr^{80} and HBr^{80m} . In the light of the preceding discussion most Br^{80} , Br^{80m} , BrBr^{80} and BrBr^{80m} would probably not be extracted into the pure water medium and thus could not contribute to any isotope effect.

Very recently Apers and Capron (87) have reported using a new technique of purification and extraction with alumina. Their results indicate that there is no difference in the per cent retention for Br^{80m} and Br^{80} produced by slow neutrons in n-propyl bromide, but that there is a difference when the activities are produced by fast neutrons.

Hamill and Williams (88) investigated the possibility of radiation damage as a cause of any variation in retention which might occur for the (n,γ) reaction in CCl_4 systems. These workers were of the opinion that scavenger reactions occur homogeneously throughout the system, and thus they felt that there should be a competition for active atoms between the additive and the molecular fragments from γ -radiation. Since no variation in yield was noted for variable amounts of γ -radiation in the CCl_4 - Cl_2 system it was concluded that such damage is of negligible importance in determining the retention. They stated that in CCl_4 the following conclusions could be made. (1) 70% of the recombination reactions were "high-

energy" processes not affected by additives. Twenty-five per cent were considered to be organic and forty five per cent, inorganic. (2) Thirty per cent involved thermal diffusion type reactions with radicals which had been produced by the atom before it became thermalized. (3) Inorganic products might eventually react with the solvent through very slow exchange processes. (This is a possibility which may partially account for the increased organic yields observed by Chien and Willard (83) for long irradiations of the propyl bromides.) (4) Inorganic products might react with impurities not removed in the purification. (5) Inorganic products might react with impurities produced by radiation damage. (6) The relatively slow reactions (3), (4), (5) could be eliminated by the presence of less than 10^{-4} mole fraction of added chlorine. All these postulates are now fairly well accepted by most workers in the field.

Libby and Fox (2), and Rowland and Libby (84) have reported the existence of an isotope effect in the (n,γ) activation of solid alkyl bromides. Br^{82} was found to have a higher organic yield in the crystalline solid state irradiations at -196°C . than $\text{Br}^{80\text{m}}$ and Br^{80} . This effect was found to be absent in the liquid state and in the case of four alkyl bromide glasses tested at -196°C . The authors felt that the initial recoil energy of the $\text{Br}^{80\text{m}}$ would be greater than that of the Br^{82} and, thus, the $\text{Br}^{80\text{m}}$ would produce a larger molten volume in the solid. In this larger molten volume the recoil atom would have a greater chance of losing its energy before it reached the semi-molten edge of the liquidous volume where the greatest increase in yield was expected. This recoil energy postulate has been tested in the photomuclear studies and the results will be reported in a later section.

More recently Hall and Sutin (89) have reported isotope effects in the irradiation of triphenyl stibine with neutrons. They have reported that the ratios of the various products for Sb^{122} and Sb^{124} vary from 1.37 ± 0.01 for triphenyl stibine to 0.88 ± 0.01 for the elementary antimony. They have noted a smaller retention of arsenic in irradiated triphenylarsine than of antimony in triphenylstibine and claim that the results are consistent with the above theory of Libby and coworkers (2,84). Their claim is based on the fact that arsenic should have a maximum recoil energy of about 288 ev while that for antimony should be only 134 ev.

Capron and Oshima (90) have given a theoretical treatment in which they showed that the initial recoil energy of "hot-atoms" could not be determined from the amount of retention.

Chemical Effects of Photonuclear Activation

Very few investigations involving photonuclear activation have been carried out probably because of the lack of availability of sources of highly energetic γ -rays and the concern over radiation damage.

Barkas et al (91) were the first to use a photonuclear activation method. They were interested in a Szilard-Chalmers type of separation of the activities produced by the (γ, n) reaction on the bromine in ethyl bromide. They observed a separation of Br^{78} , Br^{80m} and Br^{80} when ethyl bromide was irradiated with γ -rays produced by the irradiation of lithium with protons. In this case the impinging γ -rays had an energy of 17 Mev. If the energy of the γ -ray is neglected the recoil energy is given by the following relation:

$$E_M = E_m \left(\frac{M}{M} \right)$$

where m is the mass of the neutron and M , the mass of the recoiling atom. It was computed that the recoil energy for 17 Mev γ 's was about 0.11 Mev. For such an energy there is no question that bond rupture would take place.

Holmes and McCallum (92) carried out a (γ, n) reaction on Cu^{63} in copper salicylaldehyde-*o*-phenylenediimine. They obtained results quite similar to those obtained by Duffield and Calvin (93) using the (n, γ) reaction on the same compound.

Recently Rowland and Libby (94) have observed the chemical effects of the $\text{C}^{12}(\gamma, n)\text{C}^{11}$ reaction in solid and liquid CO_2 . In the case of the solid the yields of C^{11}O and C^{11}O_2 were about equal, but for the liquid at 25°C . the ratio is about 20 to 1 in favor of C^{11}O . Powdered NaHCO_3 gave results similar to dry ice, while aqueous solutions of NaHCO_3 and Na_2CO_3 gave results much like those for liquid CO_2 . In both cases the solid appears to have done a better job of confining the thermalized C^{11} atoms in the vicinity of O and O_2 fragments than the liquid, the result being that the reaction did not stop at the CO stage but went all the way to CO_2 .

Collins (95) has recently carried out an investigation of the chemical effects of the (γ, n) reaction on solid cobaltic hexamines. His results are quite similar to those determined earlier by Zuber (96) for the (n, γ) reaction on the same system. However, an apparent greater amount of fragmentation has been noted in the case of the (γ, n) activation. This would be expected because of the much greater recoil energy inherent in the case of the (γ, n) reaction.

Recently Schuler (97) has studied the chemical effects of (d, p) , $(n, 2n)$ and (γ, n) activation in liquid methyl and ethyl iodides. He reported the same organic yields for the $\text{I}^{127}(\gamma, n)\text{I}^{126}$ reaction as had previously been reported (80) for the $\text{I}^{127}(n, \gamma)\text{I}^{128}$ reaction, respectively, in methyl and

ethyl iodides. Even more recently Schuler and coworkers (98) have reported that the per cent retentions resulting from both $I^{127}(n,2n)I^{126}$ and $I^{127}(n,\gamma)I^{128}$ reactions in solid alkyl iodides are very similar. It is their belief that the initial recoil energy and other variations of nuclear processes are of little importance to the final chemical state of the recoil atoms. These results will be discussed later in connection with the results obtained in the photonuclear studies of this thesis.

It is hoped that the photonuclear studies reported hereafter will go a little way in tying off a few of the many loose ends which still exist in the field of "hot-atom" chemistry.

The investigation has been patterned after the (n,γ) studies on the propyl bromides by Libby and Fox (2). Comparative data has been taken in the photonuclear studies for many aspects of the (n,γ) work of Libby and Fox. In addition other phases of the system, such as the effects of added bromine and α,β -dibromoethylene have been studied. It is felt that the recent work of Chien and Willard (83) concerning radiation damage effects and the work of Schuler (97,98) should add credence to the data to be reported in this thesis. Only very slight radiation effects have been apparent in the present studies. In fact, as one will note, the results which will be reported are in many respects strikingly similar to the results which have been obtained in the earlier neutron studies.

EXPERIMENTAL TECHNIQUES

Purification

As had been indicated by previous workers (2,82,84) it was found necessary to subject the propyl bromides to an extensive purification treatment in order to remove any olefin impurities which might be present.

It was found that shaking the propyl bromide with ten successive portions of concentrated H_2SO_4 for a total period of one week apparently did not entirely remove impurities. The tenth portion of H_2SO_4 still turned slightly dark upon extended shaking. This may have been the result of a photochemical reaction.

Reproducible results were not obtained with propyl bromides which were purified by techniques which had previously been reported (2,82,84).

The following treatment of propyl bromides obtained from Columbia Organic Chemicals Company appeared to be adequate: (1) Ozone was passed through the propyl bromide for at least twenty four hours to tie up minute amounts of olefinic impurities. (2) The propyl bromide was vacuum distilled from an ice bath to remove ozonides which are sometimes explosive at higher temperatures. (3) The distillate was shaken twice with 3% H_2O_2 , each time for 30 minutes. (4) The propyl bromide was shaken with a dilute solution of NaHCO_3 to remove acids. This was done until no yellow coloration could be noted in the aqueous layer. (5) It was shaken with water and then dried with anhydrous sodium sulfate to eliminate any decomposition which might result when concentrated sulfuric acid was shaken with the propyl bromide. (6) The dried propyl bromide was shaken with successive portions of concentrated H_2SO_4 . Three shakings seemed to remove the maximum amount

of impurities. Any further shaking always resulted in a slight coloration of the H_2SO_4 layer of about the same color intensity. (7) To remove any excess acid the propyl bromide was shaken with a dilute solution of NaHCO_3 until no further evolution of CO_2 was noted. (8) It was then shaken with distilled water and dried with anhydrous sodium sulfate. (9) The next and critical step was to allow the propyl bromide to set overnight with 0.75 mole % Br_2 . (10) The bromine step was followed by shaking with a dilute Na_2SO_3 solution to remove the bromine and then by washing with distilled water and drying with anhydrous Na_2SO_4 . (11) The final step was distillation through the five-foot helix-packed fractionating column shown in Figure 1 which had approximately 25 theoretical plates. A technique of allowing the column to operate at total reflux with intermittent takeoff was used until no drop in head thermometer temperature was noted following the taking off of a distillate sample. When this state was reached the takeoff was continuous until a change in refractive index or boiling point was noted.

The criteria for purity were constant boiling temperature and refractive index of the distillate. The refractive indices were measured on a Bausch and Lomb Precision Refractometer and are listed in Table 1.

Ethyl, methylene, ethylene, propylene and trimethylene bromides were subjected only to the sulfuric acid, NaHCO_3 , distilled water, and Na_2SO_4 treatment followed by distillation through the five foot column. Methylene, ethylene, propylene, and trimethylene bromides were fractionated at pressures in the range of 100mm Hg. The measured n_D^{20} values as compared to literature values are found in Table 1.

The bromine was obtained from Baker Chemical Company and was used without further purification. The α,β -dibromoethylene was obtained from Eastman Organic Chemicals Company and was also used without further treatment.

Figure 1. Fractional distillation apparatus

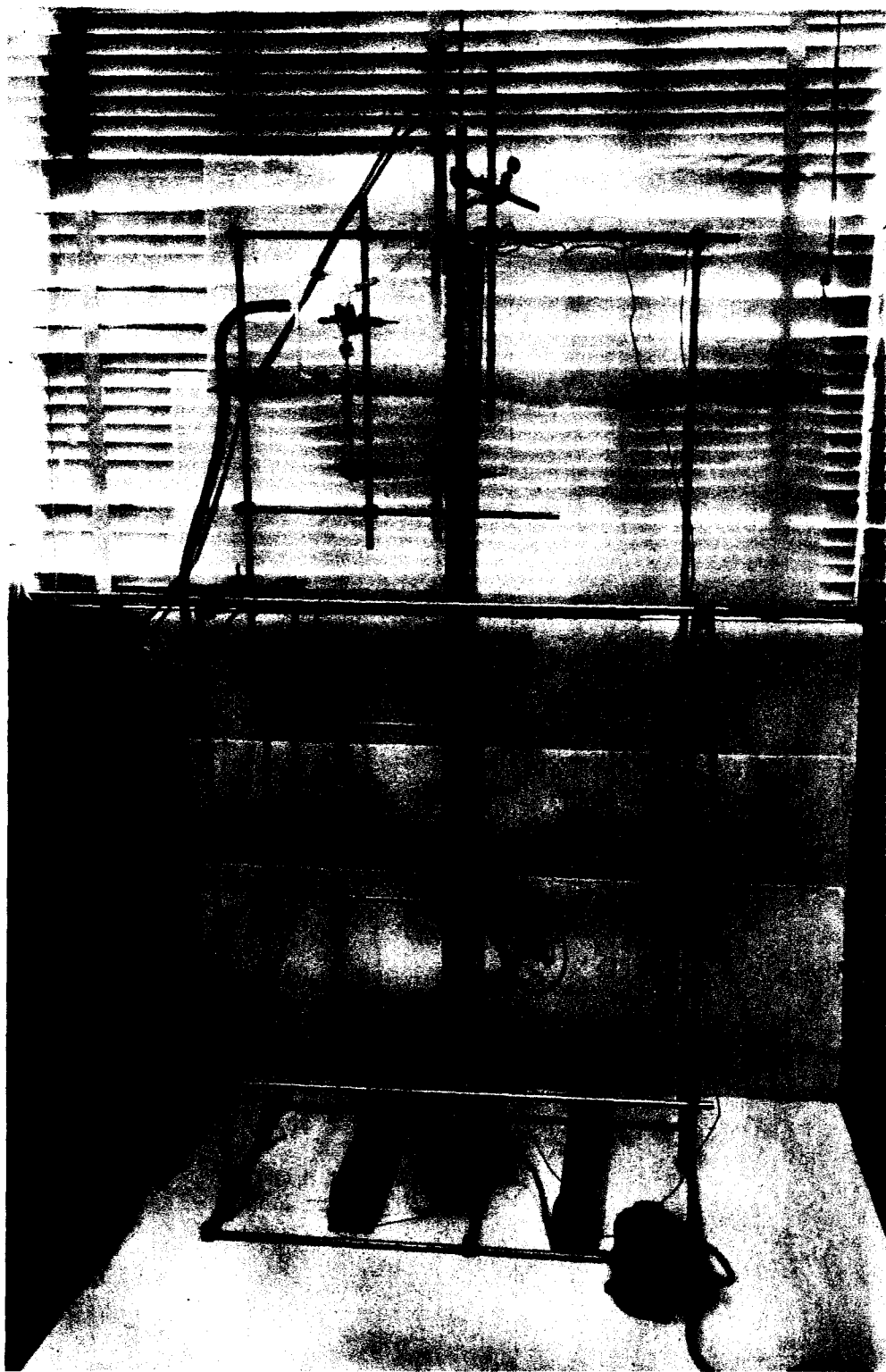


Table 1
Refractive Indices

Compound	n_D^{20}	
	Literature Values	Measured Values
n-Propyl bromide	1.4341	1.4339
iso-Propyl bromide	1.4251	1.4252
Ethyl bromide	1.4239	1.4241
Methylene bromide	-	1.5411
Ethylene bromide	1.5379	1.5385
Propylene bromide	1.5203	1.5199
Trimethylene bromide	1.523	1.5231

Extraction

One of the main facets of "hot-atom" chemistry studies on organic bromides is to remove by means of aqueous extraction those radiobromine atoms which end up in an inorganic form. The techniques used here were very similar to those which had been used previously, the extracting solution being a dilute aqueous solution of Na_2SO_3 . Approximately 0.1 g of H_3AsO_4 and 0.560 g of NaBr were added per liter of Na_2SO_3 solution as carriers for arsenic and bromine activities. It was very important to make sure that enough Na_2SO_3 was present to reduce all of the inorganic radiobromine atoms to the water soluble bromide state. When appreciable amounts of bromine were present as scavenger, it was necessary to add crystalline Na_2SO_3 during the shaking process until all of the bromine

color had been eliminated. It was evident that pure water would not remove a significant portion of any bromine which was still in the elemental state.

Two successive ten minute extractions using freshly prepared Na_2SO_3 solution appeared to remove better than 99% of the extractable activity from the organic layer. Varying amounts of Na_2SO_3 in excess seemed to have no effect on the organic retention. When no bromine was present as scavenger or carrier the second extraction contained between one and three per cent as much activity as the first. However, when bromine was present the second extraction contained less than one per cent of the total.

Fractional Distillation

It was decided that any study involving a determination of the various organic yields produced would require a means of separating all carriers into pure fractions.

The five-foot helix-packed fractionating column of about twenty five theoretical plates shown in Figure 1 was constructed (99). It was found necessary to equip the column with a vacuum attachment since the column tended to flood at temperatures of 110°C . or higher and this flooding could only be prevented by keeping the temperature down or using an exceedingly slow rate of throughput. It was also desirable to distill the dibromides at lower temperatures to reduce decomposition.

For runs in which the yields of the various organic products were desired the extracted organic liquid was added to a mixture of the various carrier compounds to be used. Twenty ml each of ethyl, n-propyl, iso-propyl, methylene, ethylene and trimethylene bromides and thirty ml of propylene bromide were mixed in the still pot of the column.

In order to obtain the desired degree of purity with the column it was necessary to fractionate almost continuously over a 40 hour period. The intensity of the γ -source was adequate to produce enough $\text{Br}^{80\text{m}}$ activity so that some could still be detected in the various fractions after 40 hours.

Methyl bromide and ethylidene dibromide (1,1 dibromoethane) were semi-quantitatively detected by noting peak counting rates between pure carrier fractions. No other peaks than these were noted. This and the fact that the sum of the determined yields accounted very closely for all organic activity indicated that no important compounds had gone unnoticed. The total yield of higher boiling "polymers" was determined by subtracting the yield of trimethylene bromide from the yield obtained for the final fraction in the still pot.

In a forty hour fractionation it was possible to get enough of each carrier compound of better than 95% purity for counting. The criteria for purity of distillate samples were constant boiling temperatures, and refractive indices in agreement with the values previously determined for the pure carriers.

Radioactivity

The counting of radioactivity was complicated by the fact that several long-lived activities other than $\text{Br}^{80\text{m}}$ (4.6 hr) were produced by the high energy γ -rays. Since C^{11} (20 min) was produced by (γ, n) on C^{12} no study on Br^{80} (18 min) could be made and it was necessary to wait for about 3 hours to allow these two activities to die out before the $\text{Br}^{80\text{m}}$ (4.6 hr) could be counted. Br^{78} (6 min) was produced by (γ, n) on Br^{79} but decayed out in about one hour. Other photonuclear reactions which took place were $\text{Br}^{79}(\gamma, 2n)\text{Br}^{77}$, $\text{Br}^{79}(\gamma, 3n)\text{Br}^{76}$, $\text{Br}^{81}(\gamma, \alpha n)\text{As}^{76}$, and $\text{Br}^{79}(\gamma, \alpha n)\text{As}^{74}$. (See

Figures 3, 4 and 5.) For most of the counting employed the latter four activities gave negligible counting rates compared to the counting rate of the $\text{Br}^{80\text{m}}$.

The Iowa State College Synchrotron was the source of γ 's for the present work. It was operated at full power in which the maximum energy of γ 's was 60 to 70 Mev. However, the distribution of energies is such that only a small fraction of the γ 's have energies approaching the maximum. The intensity of the beam varied from about 300 roentgens per minute to 1000 roentgens per minute and was adequate to produce upwards of several million disintegrations per minute zero-time activity of $\text{Br}^{80\text{m}}$ for a four hour irradiation on a 25 ml sample of propyl bromide.

The propyl bromides were irradiated by placing them in a 25 mm by 200 mm Pyrex test tube with a cork-stopper and immersing the test tube in a Dewar flask. A stopper was then placed in the Dewar, making a very nearly light tight system. The temperature of the propyl bromide which was irradiated could be controlled by the addition of the appropriate liquid or liquid-solid mixture to the Dewar flask. The Dewar flask was then placed directly in the path of the synchrotron beam, so that the beam passed through the propyl bromide in the test tube.

In the runs to determine the various radionuclides which were produced irradiation times of twelve hours or more were used. For runs to determine the yields of organic products irradiation times of from 3 to 12 hours were used. A compromise between the amounts of activity and radiation damage was desirable. Because the intensity of the beam was at times quite variable the length of irradiation time sometimes had to be extended beyond the optimum 3 to 4 hour irradiation time.

For runs in which only retention versus extraction data on $\text{Br}^{80\text{m}}$ was taken the samples were irradiated twenty to thirty minutes.

All samples were counted in Nucleonic Corporation of America model GM-4 counting tubes with annular jackets of 5 to 7 ml capacity. The thickness of the glass wall between sample and tube was about 30 mg/cm^2 . These tubes, ordinarily used for flowing liquids, were adapted for counting stationary samples by bending the entrance and exit tubes so that they both extended in the same vertical direction.

The $\text{Br}^{80\text{m}}$ activity was counted by means of the 2.0 Mev beta of the Br^{80} daughter, and it was found that the relative counting efficiency of the counting tubes decreased as a function of the density of the liquid counted. The variation of counting efficiency with density was very nearly the same for all five counting tubes used in this work. Apparently variations in wall thicknesses of the tubes and other factors had little effect. The values of relative counting efficiency for the various densities of compounds used are listed in Table 2. The density correction for counting rate was made by dividing the value of relative counting efficiency at the given density into the measured counting rate. For a further discussion of the effect of liquid density on counting efficiency see the discussion by Chiang and Willard (100).

In the process of taking pure samples off the column it was sometimes desirable to count more than one sample of a given compound. When this was done it was necessary to increase the volume of the individual samples enough to fill the counting tubes. The liquid added in each case was identical in composition to the sample taken off the column except that it contained no activity. Since the activity was always diluted when this was done, it was necessary in such cases to apply a correction factor for the dilution.

Table 2

Relative counting efficiency as a function of density of liquid counted

Compound	Density, g/cm ³	Relative Counting Efficiency for Br ^{80m}
Water	0.997	1.12
iso-Propyl bromide	1.310	1.01
n-Propyl bromide	1.353	1.00
Ethyl bromide	1.460	0.97
Propylene bromide	1.933	0.875
Trimethylene bromide	1.987	0.865
Ethylene bromide	2.180	0.82
Methylene bromide	2.495	0.74

In order to estimate the amount of methyl bromide it was necessary to count three successive pure fractions of ethyl bromide. A curve of counting rate of the three successive fractions as a function of ml of ethyl bromide taken over always showed a large decrease from the first to the second fraction. The slope of the curve from the second to the third fraction was nearly zero, indicating that very little methyl bromide remained in the third fraction. Such behavior is expected because no methyl bromide carrier was added and methyl bromide is much more volatile than ethyl bromide. The methyl bromide activity could be estimated by subtracting off the activity of the ethyl bromide. If the fraction of the total methyl bromide coming over in a given sample was determined, then the yield of the methyl bromide could be estimated.

A similar technique was employed for determining ethylidene bromide (1,1 dibromoethane) which has a boiling point intermediate between those of methylene and ethylene bromides.

Because of the presence of the longer-lived activities, it was necessary to follow the decay at all times so that time corrections could be made for all samples counted. It was found that even when samples of varying density were counted all curves were very nearly parallel for the first forty hours. The assumption was therefore made that parallel curves could be drawn through the counting rates for all samples and then the relative yields determined by taking the counting rate of each at a specified time and then applying the appropriate density correction. Figure 2 is a typical set of such curves.

In each case the total organic yield was determined by saving a portion of the extracted propyl bromide for counting. The decay curve of this sample served as the basis for drawing all other parallel curves. It was possible then to determine if all the organic activity was accounted for. This was done by summing up all the various yields and noting how well the sum agreed with the total organic yield as determined from the unfractionated sample. The agreement was such that it was felt that density corrections were close to being correct, that the longer lived activities did not appreciably affect the determination of $\text{Br}^{80\text{m}}$ yields, and that all products of importance were accounted for. The work of Libby and Fox (2) is in agreement with this last assumption. Recent work by Evans and Willard (5) concerning a gas phase chromatography method which indicates a greater multiplicity of products will be discussed further in a later section.

Any Br^{80} which had reacted with the glass walls as a result of its high positive charge from the $\text{Br}^{80\text{m}} \rightarrow \text{Br}^{80}$ transition could not be removed by

cleaning. Thus a sample of very low activity could not be counted with any degree of accuracy immediately after the counting of a sample of high activity. If the sample of high activity were in the counting tube for ten minutes or longer, it would leave a considerable number of non-removable Br^{80} atoms on the walls of the tube. The only thing that could be done in such a case was to wait for the unwanted activity to die out.

Other than for the above limitation the counting tubes could be cleaned very quickly and easily. After counting an organic liquid several portions of absolute alcohol were washed through the tube, and it was then dried by attaching it to an aspirator and sucking air through it. When an aqueous sample had been used distilled water was passed through the tube prior to the alcohol treatment.

It was very important in counting the various samples to make sure that the Br^{80} daughter was in equilibrium with Br^{80m} . This could easily be checked by counting the sample until it followed the 4.6 hour rate of decay. Certain aspects of the fractionation process seemed in many cases to disrupt the equilibrium and gave an initial excess or deficit of Br^{80} . Of course, some of the excess was due in many cases to Br^{80} activity remaining on the tube walls from the previous sample.

On runs in which it was desirable to observe long decay curves counting was done continually using a Streeter-Amet Printer. This gave a continuous record of the counting rate at fifteen or sixty minute intervals during the time the decay was followed.

The arsenic activities were determined by precipitating AgBr from the aqueous solution which contained H_3AsO_4 as a holdback carrier. AgAsO_4 was soluble in the dilute nitric acid solution which was used to precipitate the AgBr . The liquid solution was then counted and the decay of arsenic noted.

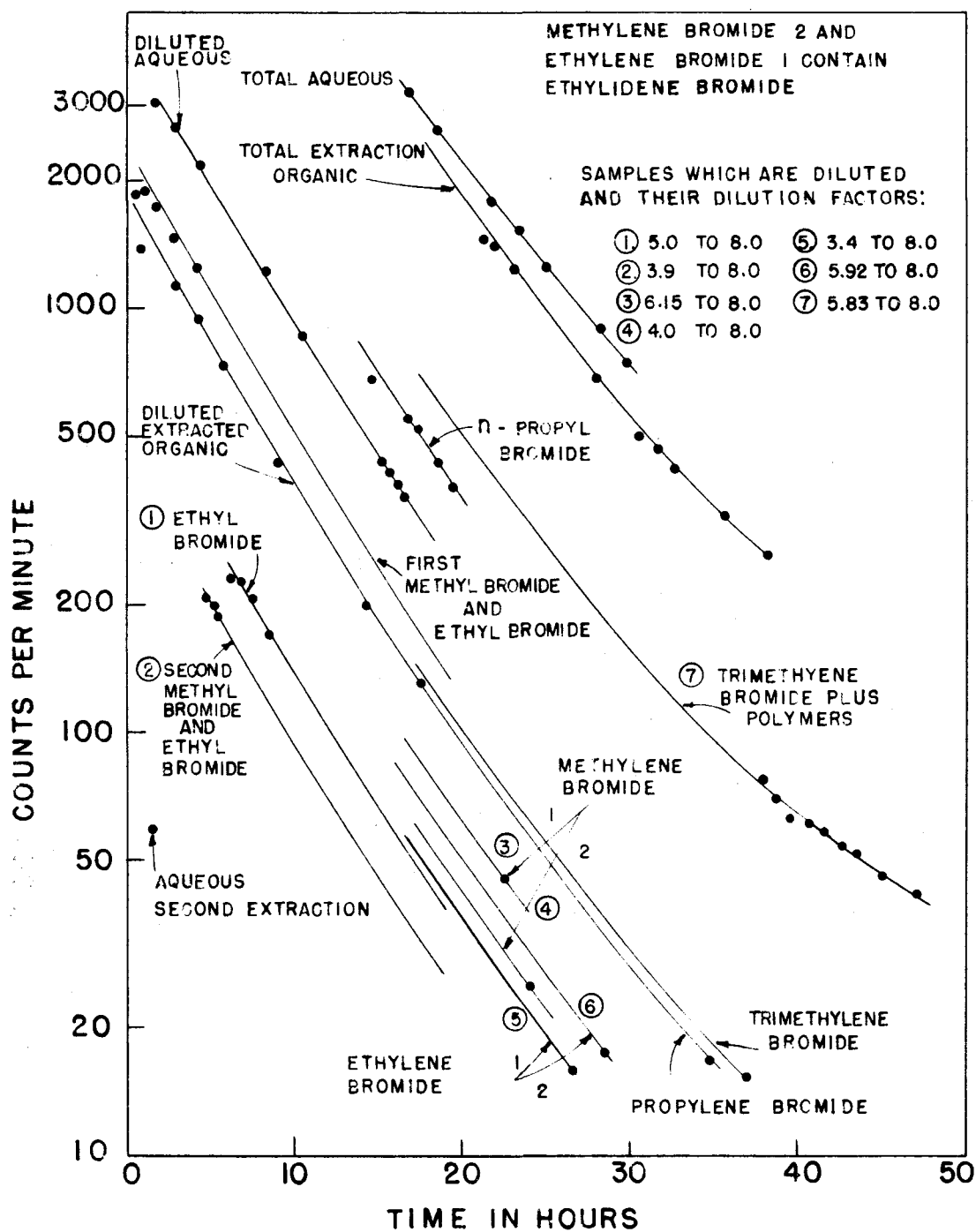


Figure 2. Yield curves for the various products formed in liquid n-propyl bromide containing 4.7 mole % Br_2 at 0°C .

Since no arsenic activity remained in the propyl bromide after extraction it was possible to follow the decay of the extracted propyl bromide and then analyze the curve for the various bromine activities.

EXPERIMENTAL RESULTS

Radionuclides Produced

As was stated earlier radionuclides other than 4.6 hour $\text{Br}^{80\text{m}}$ were produced by the high energy γ -rays. Because of the parallel nature of the yield curves in the first forty hours of decay it was felt that these other activities were not appreciably affecting the values of the various yields for $\text{Br}^{80\text{m}}$. However, the very fact that $(\gamma, 2n)$ and $(\gamma, 3n)$ reactions might exist was very intriguing. The reason for this was that although all such (γ, xn) type reactions would give rise to bromine isotopes, each product nuclide would be expected to have a different initial recoil energy as well as different collision properties by virtue of its slightly different mass. A comparison of organic retention yields for Br^{76} , Br^{77} and $\text{Br}^{80\text{m}}$ might give an interesting insight into the mechanisms involved when the recoil atoms reenter chemical combination.

Considering the importance of data comparing chemical effects of the various photonuclear reactions it was felt that an attempt should be made to completely analyze the gross decay curve into the various activities. The big limitation to such an analysis was in getting an irradiation of sufficient length and intensity to produce enough of the activities to give the required statistics.

Early runs which gave adequate activity suffered from the fact that not quite enough points were taken at critical times. However, within the statistical error these curves could always be varied enough to be analyzed into the five activities which have already been mentioned.

Figures 3, 4, and 5 represent the results of the final long irradiation which was carried out. It was of fourteen hours duration at an average beam

intensity of about 500 roentgens per minute. To get a high organic yield, solid n-propyl bromide at -196°C. was irradiated. Such a system gave rise to an organic yield of about 85% for $\text{Br}^{80\text{m}}$. The decay was then followed using a Streeter-Amet Printer which gave a continuous record of the counting rate in 60 minute intervals over the period that the decay was followed.

Figure 5 represents the gross decay of the unextracted n-propyl bromide and, as can be seen, has been analyzed as the sum of five straight line decays.

Figure 3 represents the decay of the two arsenic activities produced by $(\gamma, \alpha n)$ reactions (101). It was possible to get such a sample since all arsenic was extracted into aqueous medium. All bromine activity could then be removed from the aqueous extracting solution by precipitating AgBr in a dilute HNO_3 solution. The arsenic remained in solution, presumably as AsO_3^{---} or AsO_4^{---} , and was counted in a liquid counting tube. The decay curve shown in Figure 3 was followed only long enough so that the 17.5 day rate of decay was apparent for several days. In two earlier runs the decay of 17.5 day As^{74} had been followed for over a month and its existence established.

Figure 4 represents the decay of extracted n-propyl bromide. Since all arsenic was extracted into the aqueous layer, it was possible to establish the three bromine activities by analysis of the decay of the extracted sample. In some early runs it sometimes appeared that a very small amount of 35.6 hour Br^{82} was present. This tended to make the decay curve difficult to analyze. The effect was not noted in the final decay curve shown in Figure 4. In earlier runs the 57 hour activity had been established by counting for several half lives, so in this particular run the decay was only followed long enough to get a good determination of the 57 hour decay line. In this final run the apparent 56.3 hour rate of decay when subtracted

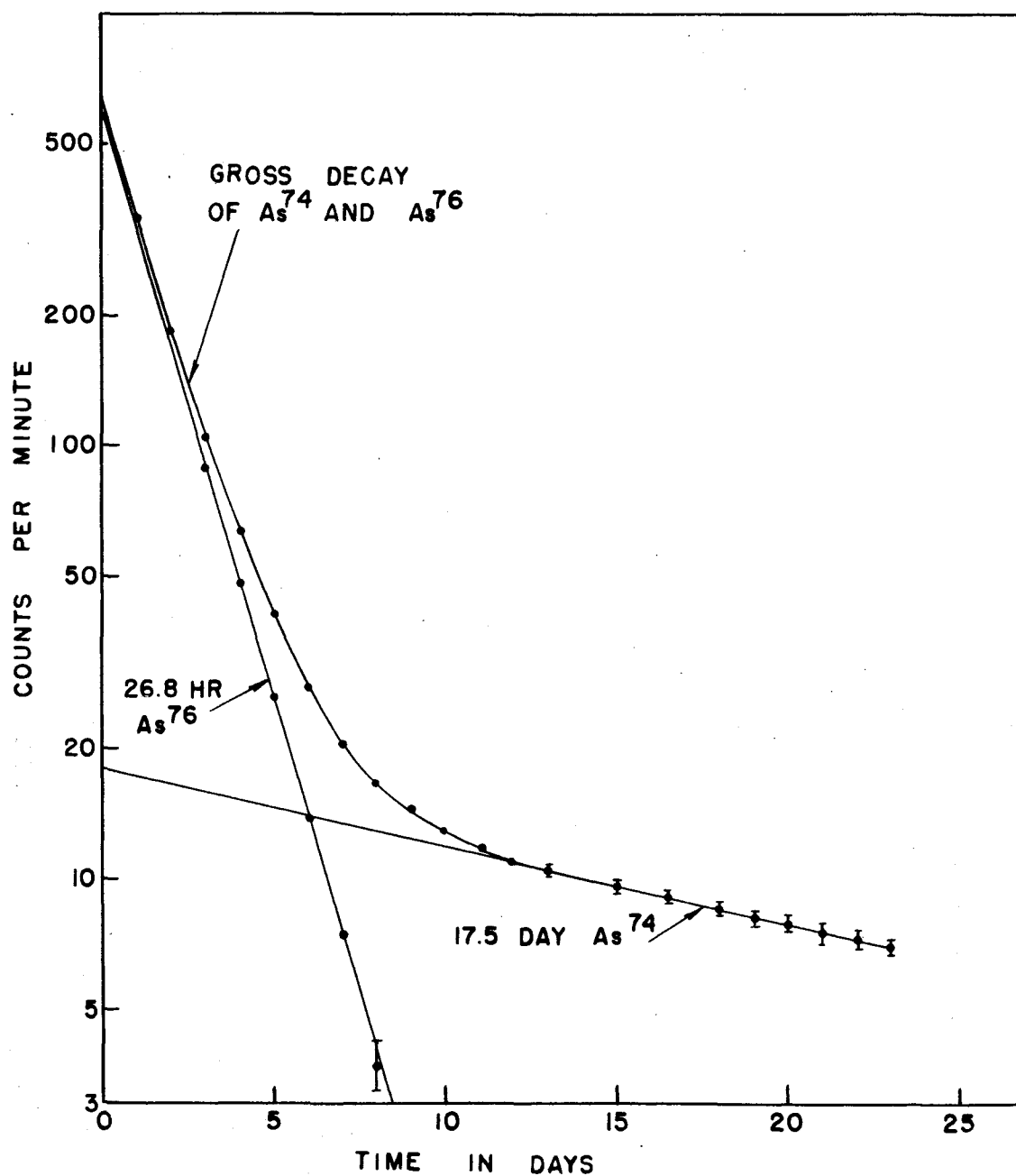


Figure 3. Analysis of gross arsenic decay curve into the As^{74} and As^{76} activities formed by photonuclear reactions from Br^{79} and Br^{81} .

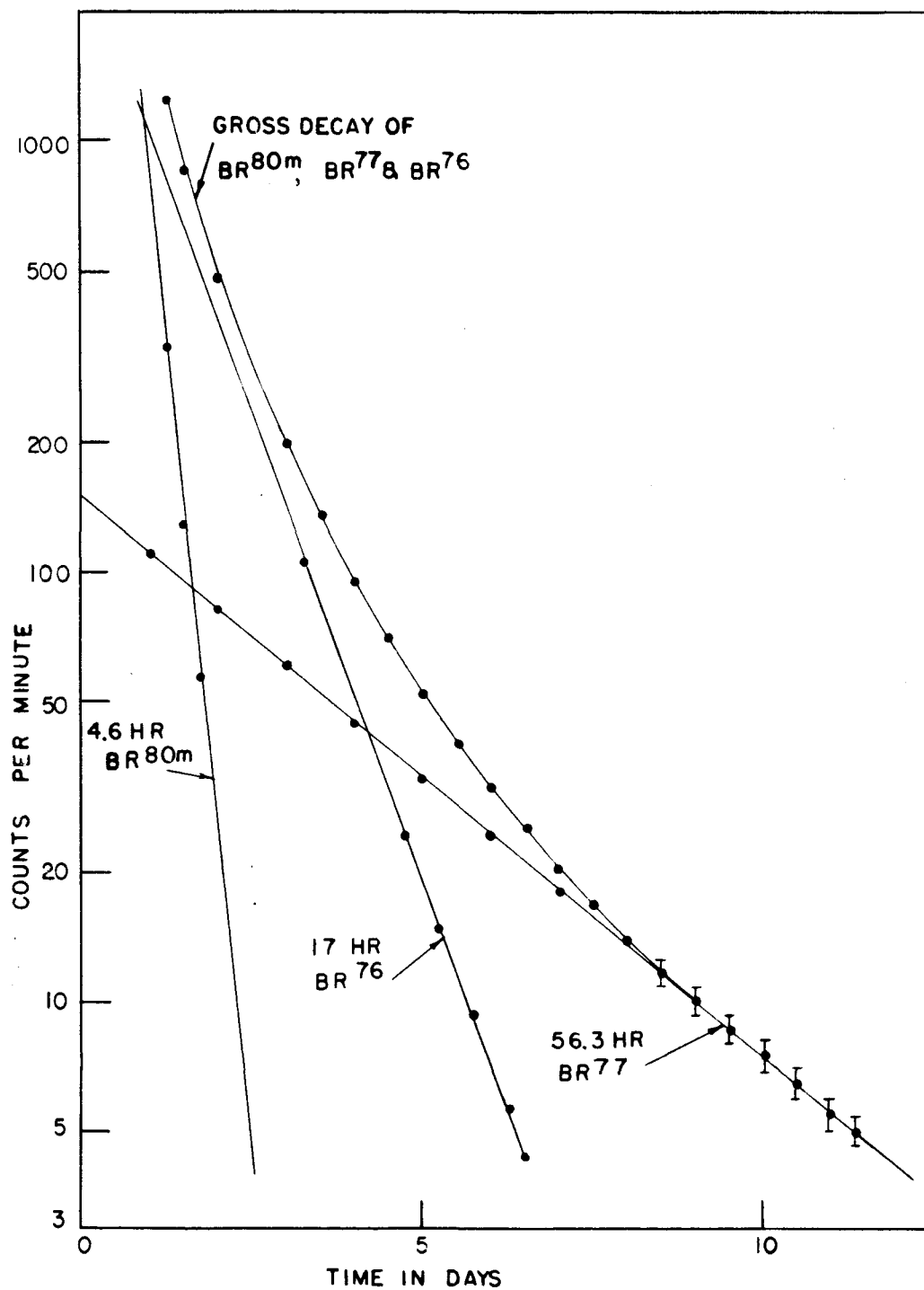


Figure 4. Analysis of gross bromine decay curve into the Br^{80m}, Br⁷⁶ and Br⁷⁷ activities from photonuclear reactions on Br⁸¹ and Br⁷⁹.

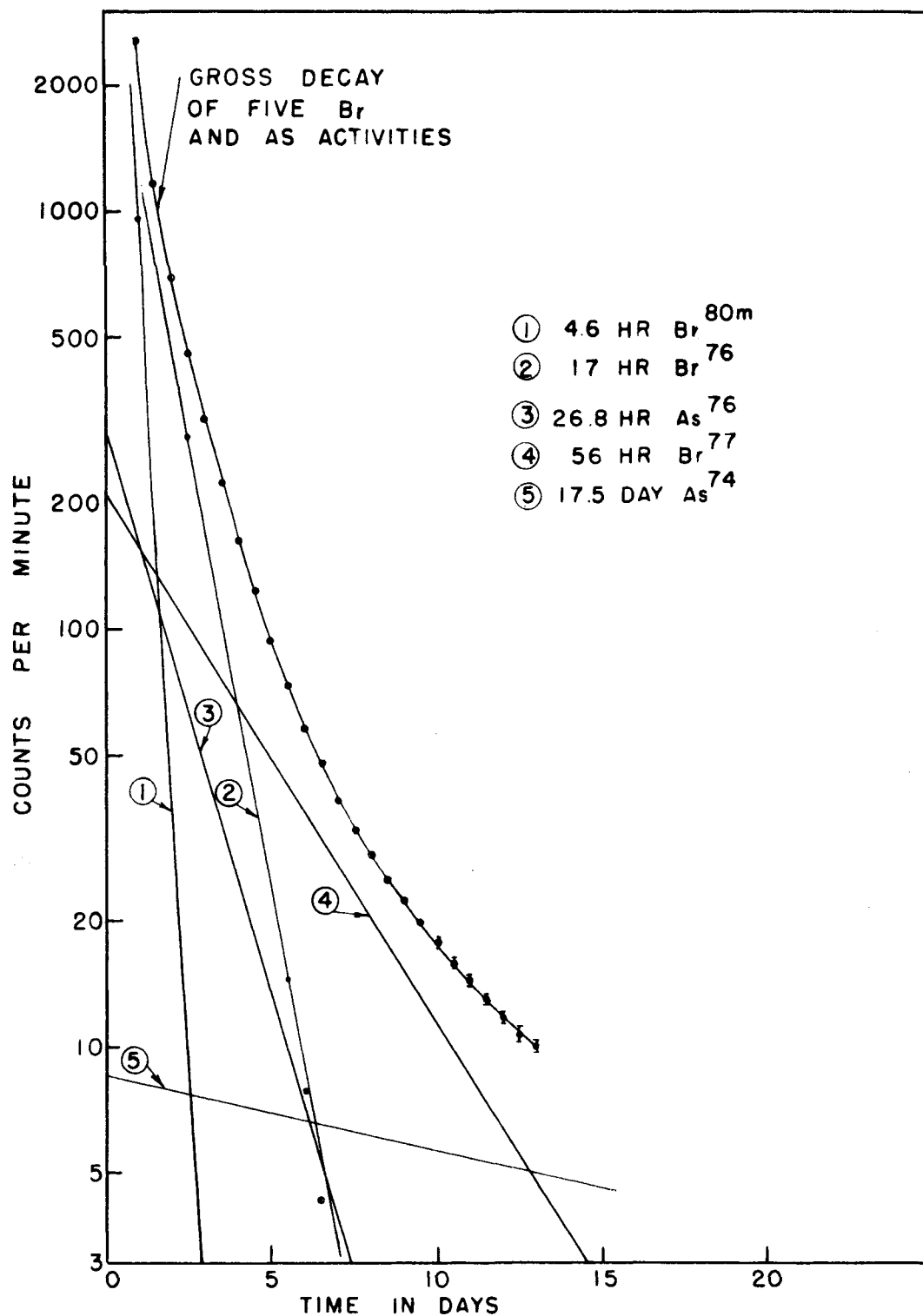


Figure 5. Analysis of gross decay curve into the Br and As activities formed by photonuclear reactions on Br⁷⁹ and Br⁸¹.

gave an exceptionally good line for the Br^{76} at 17.3 hours. Both of these values are in quite good agreement with values listed in the literature.

In analyzing the curve in Figure 5 it was necessary to estimate the contribution of the arsenic activities to the gross decay. This was done by subtracting the appropriate amount of 17.5 day As^{74} from the curve such that the curve resulting from the subtraction tailed off with a 57 hour half-life. The amount of 26.8 hour As^{76} which was then subtracted depended on the amount of As^{74} which had been subtracted. Since the amount of As^{74} subtracted was about half of the amount in the arsenic decay curve (Figure 3), the amount of As^{76} subtracted was also about half the amount in the arsenic decay curve. When the 57 hour Br^{77} activity was subtracted from the resulting bromine curve a straight line was produced which extended down to about five counts per minute. This line gave a half-life of 17 hours. Subsequent subtraction of the 17 hour decay left a line which showed the 4.6 hour half-life of Br^{80m} .

Retention of Br^{80m}

Effect of Temperature and Phase in the Pure Propyl Bromides

It was felt important to determine the effect of phase and temperature in the case of the (γ, n) formation of Br^{80m} in the propyl bromides and compare the results with those of the previous (n, γ) studies. In the (n, γ) activation of the propyl bromides (2,3,84) a definite effect of phase on retention had been noted, while little or no temperature dependence had been apparent. Figure 6 shows the results of a series of (γ, n) runs at various temperatures for both n-propyl and iso-propyl bromides. There is a remarkable similarity of these results to those of Libby and Fox (2) for

the (n,γ) work on the propyl bromides. Especially important is the sharp jump in retention in going from liquid to solid phases. This effect was noted for both modes of activation.

The counting method employed to obtain reproducible results for retention runs is shown in Figure 7. The aqueous sample was counted first in a specified counting tube. It was counted long enough to insure equilibrium of 18 minute Br^{80} with its 4.6 hour parent $\text{Br}^{80\text{m}}$ and to obtain good counting statistics. The aqueous sample was then replaced with the extracted organic sample. The latter sample was counted long enough to establish the 4.6 hour rate of decay of $\text{Br}^{80\text{m}}$ and then was replaced with the aqueous sample which was counted again. In the nearly fifty such runs which were made the two curves were always noted to be very nearly parallel.

The value for n-propyl bromide at 0°C. is the average of four runs on pure n-propyl bromide containing no added Br_2 . The retention values which were determined were 48.2%, 46.7%, 46.5%, and 48.1%. The average of these values is 47.4%. Since these values were determined on samples from four different purification batches the very close agreement of the values indicates that the n-propyl bromide was adequately purified with respect to olefins. The agreement also indicates reproducible extraction and counting techniques.

In the case of liquid irradiations the accuracy of the values should be about $\pm 1\%$ retention; but because of the tendency of the propyl bromides to form glasses when being solidified, the values in the solid phase could be a few per cent low. In the case of the pure compounds in Figure 6 this is probably not so. The glass forming tendency will be discussed further in later sections.

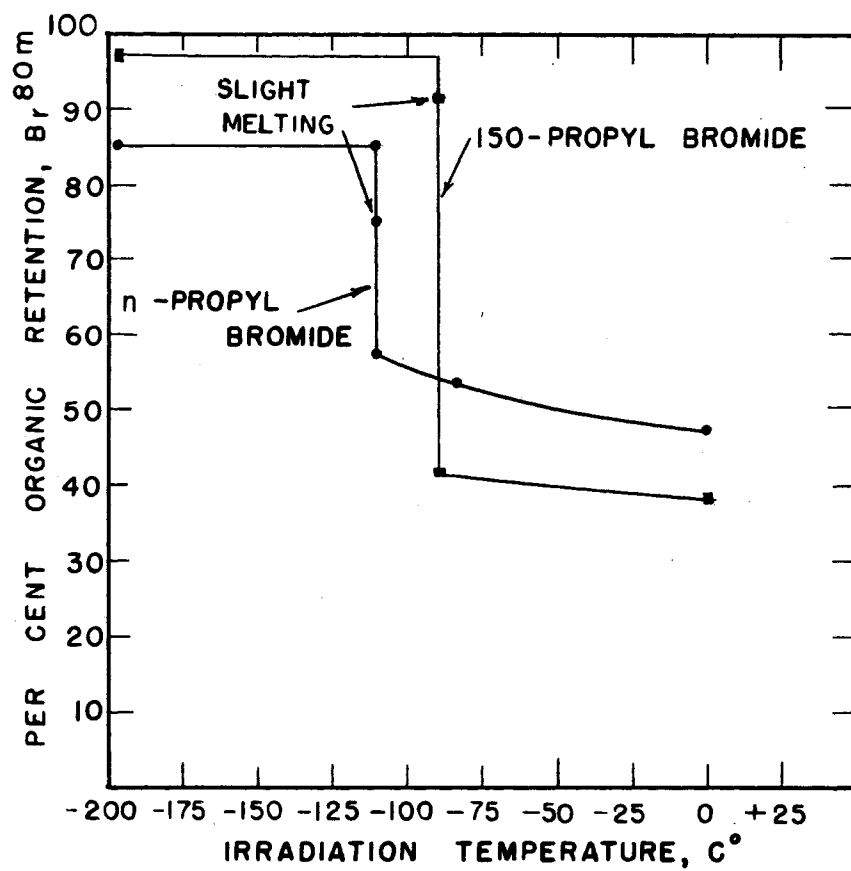


Figure 6. Temperature versus retention for $\text{Br}^{80\text{m}}$.

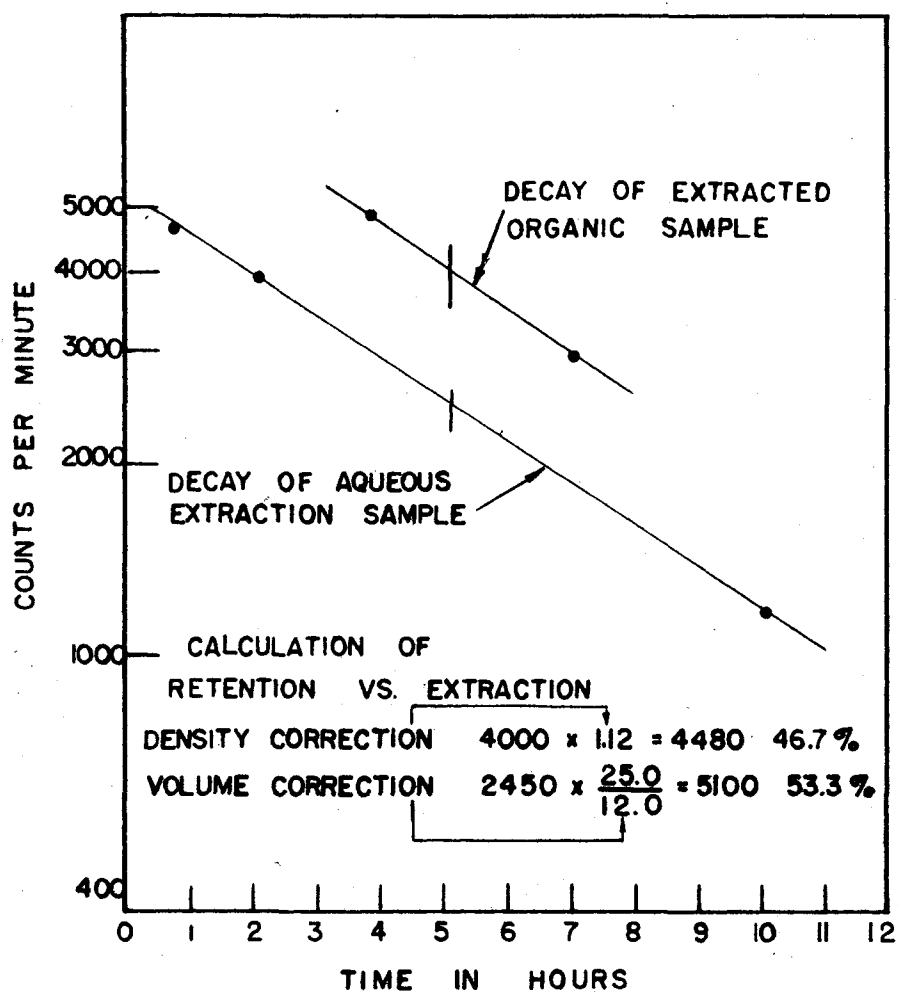


Figure 7. Retention and extraction curves showing determination of retention in n-propyl bromide at 0°C.

In Figure 7 one notes a correction for volume and one for density. The density correction was discussed earlier in the section on radioactivity. The volume correction is applied since 25 ml of aqueous solution was shaken with 12 ml of the propyl bromide. The extracted bromine would thus be more dispersed than the retained bromine. The volume correction is used to account for this dispersion.

Effect of Added Bromine in Liquid Propyl Bromides at 0°C.

To elucidate the importance of thermal type reactions it was felt necessary to observe what effects "scavengers" might have on the retention. This would be another facet of the comparison of the chemical effects of (n, γ) and (γ, n) reactions. Small amounts of Br_2 had previously been observed to markedly lower the retention in alkyl bromides activated by thermal neutron capture (52,53,80,81,82,84).

The curves in Figure 8 are felt to be as accurate as any determined in the present studies. As was suspected would be observed, the curves exhibit a steep drop with the addition of small amount of bromine, indicating the existence of thermal reactions for the (γ, n) reaction in the propyl bromides.

The fact that 0.73 mole % of added bromine gave a retention value of 42% indicates that the value of 47.4% for the pure propyl bromide is not higher than it should be as a result of olefin impurities. Such a bromine percentage should appreciably decrease the retention yield. The parallel nature of the curves for both propyl bromides seems to add credence to the accuracy of individual values. No effort has been made to indicate the limits of error on a statistical basis, since all points except 0 mole % Br_2 represent only one extraction.

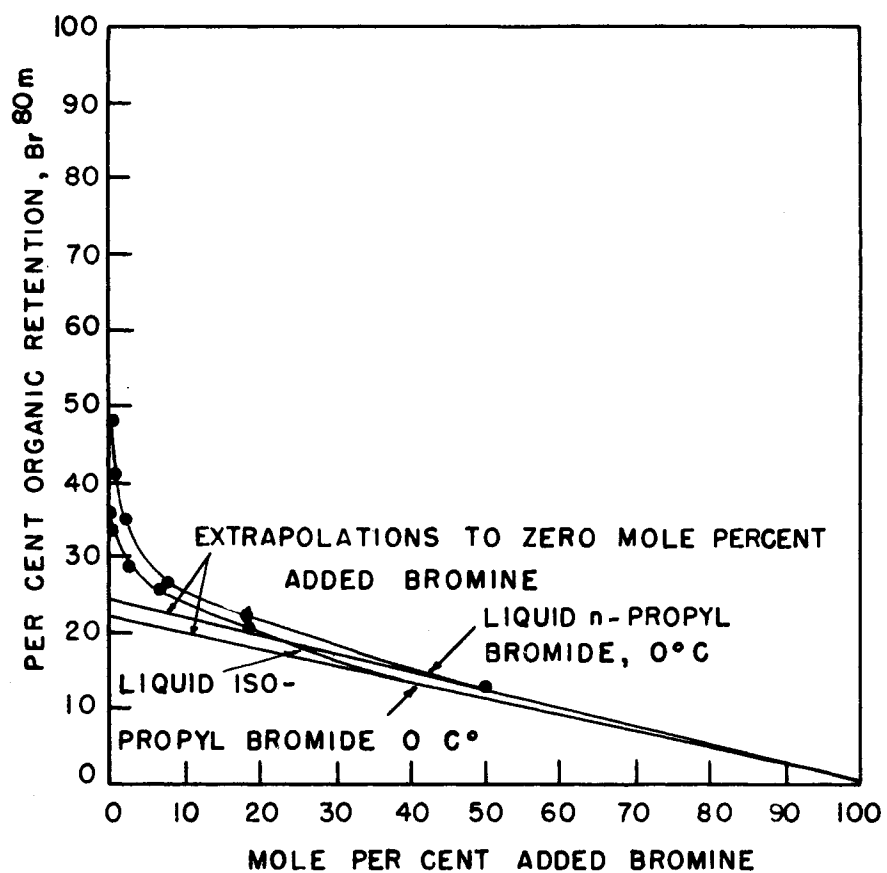


Figure 8. Retention of (γ,n) produced Br^{80m} in propyl bromides as a function of bromine concentration at 0°C.

As more bromine was added to the propyl bromide, more sodium sulfite was needed to reduce all bromine to the bromide so that it could be extracted into the aqueous medium. In the case of 50 mole % bromine about 7 ml of bromine was present in 12 ml of n-propyl bromide. When extracting such a mixture 100 ml of aqueous solution was used, and it was found that the density of the resulting solution was about 1.4 g/cm^3 . When this increased density was taken into consideration, the retention value of 12.5% shown in Figure 8 was obtained.

The 100 ml volume of aqueous solution was used when several milliliters of bromine were reduced since such large amounts of heat were given off in the reduction process. Even with 100 ml of aqueous solution it was necessary to cool the solution during the shaking process.

Although only one final run was made to determine the retention of pure iso-propyl bromide the value of 35.8% should be fairly accurate. It is noted that the value for 0.75 mole % Br_2 is 34% which indicates that the value for pure iso-propyl bromide is about right.

The extrapolations to zero bromine concentration represent approximate determinations of the retention which resulted from nonthermal or "hot" reactions. In line with the postulates of previous investigators these results indicate that about 25% of the $\text{Br}^{80\text{m}}$ retention in liquid n-propyl bromide occurs as a result of nonthermal reactions and about 22%, as a result of thermal reactions. For iso-propyl bromide the respective values are 23% and 13%.

Effect of Added Bromine in Solid Propyl Bromides at -196°C .

In an attempt to indicate possible thermal reactions in the solid phase the effect of added bromine was investigated. Figure 9 shows the effect of bromine concentration on the retention in the solid propyl bromides at -196°C . If an extrapolation to zero bromine concentration means anything, about 29% of the retention in solid n-propyl bromide and about 34% in iso-propyl bromide result from thermal reactions. The fact that such percentages are somewhat higher than one might consider possible will be discussed in a later section.

In the runs to obtain the points on the curve in Figure 9 it was found difficult to completely eliminate glass formation. Three runs for n-propyl bromide and one run for iso-propyl bromide resulted in retention values 8% to 12% below the curves shown. In all these cases, however, there was a definite glassy appearance to the solid propyl bromides. In one experiment in which a low retention was obtained the bromine appeared as red spheres suspended in the transparent and faintly red solid propyl bromide.

As a result of this tendency of the bromides to form a glass which had previously been observed by other investigators (2,84), great care was taken to obtain crystalline solidification. The samples were cooled very slowly and gave an outward appearance of yellow crystalline opacity. The fact that the points shown in Figure 9 follow the curves quite closely indicates that the crystalline state was attained throughout the mixture. However, further points should be determined as a check on those shown to make sure that they are as high as they should be.

Effect of Added α,β -Dibromoethylene in Liquid and Solid n-Propyl Bromide

The use of α,β -dibromoethylene as a scavenger for thermal bromine atoms was discussed in an earlier section. (See page 20.)

Figure 10 shows the effect observed when α,β -dibromoethylene was added to liquid and solid n-propyl bromide in increasing amounts. A very sharp rise in the retention was noted for very low mole percentages of α,β -dibromoethylene. As more scavenger was added the rise became less sharp and leveled off as was expected. The extrapolation to zero mole % added scavenger indicates that of the total organic yield of 53%, nonthermal reactions account for 28% and thermal ones for 25%.

The effect of this scavenger in the solid medium was not very noticeable. The extrapolation to zero bromine concentration in this case indicates about 12% nonthermal inorganic and 3% thermal inorganic reactions.

Relative Yields of Products Containing $\text{Br}^{80\text{m}}$

When the present investigation was initiated, it was the primary intent to gather data as exemplified by this section on yields of products. If the various products containing $\text{Br}^{80\text{m}}$ could be satisfactorily separated and counted before the $\text{Br}^{80\text{m}}$ died out, a valuable comparison between the previously reported results for the $\text{Br}^{81}(\text{n},\gamma)\text{Br}^{82}$ reaction and the (γ,n) reaction in the propyl bromides could be reported.

In connection with Figure 2 (See page 45.), which represents the run on liquid n-propyl bromide at 0°C. containing 4.7 mole % Br_2 , calculations will be given to show how such curves were used to determine percentage yields.

Counting rates for all samples were corrected to a particular time by means of the parallel curves. At 18 hours in Figure 2 the counting rate for

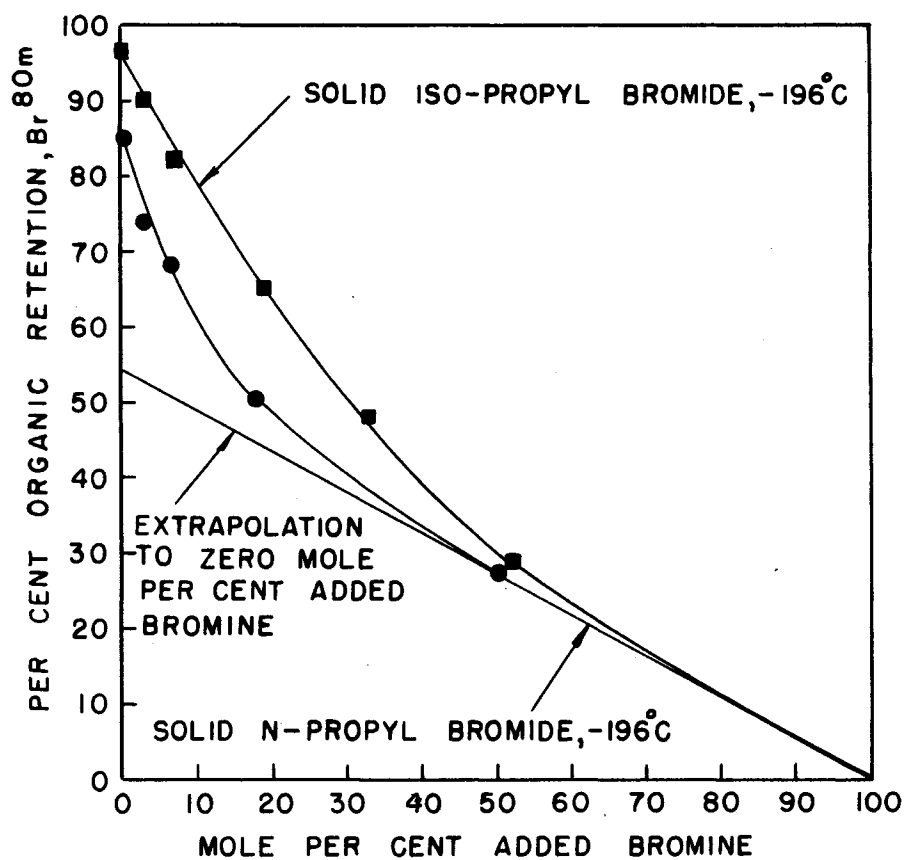


Figure 9. Retention of (γ,n) produced Br^{80m} in propyl bromides as a function of bromine concentration at -196°C.

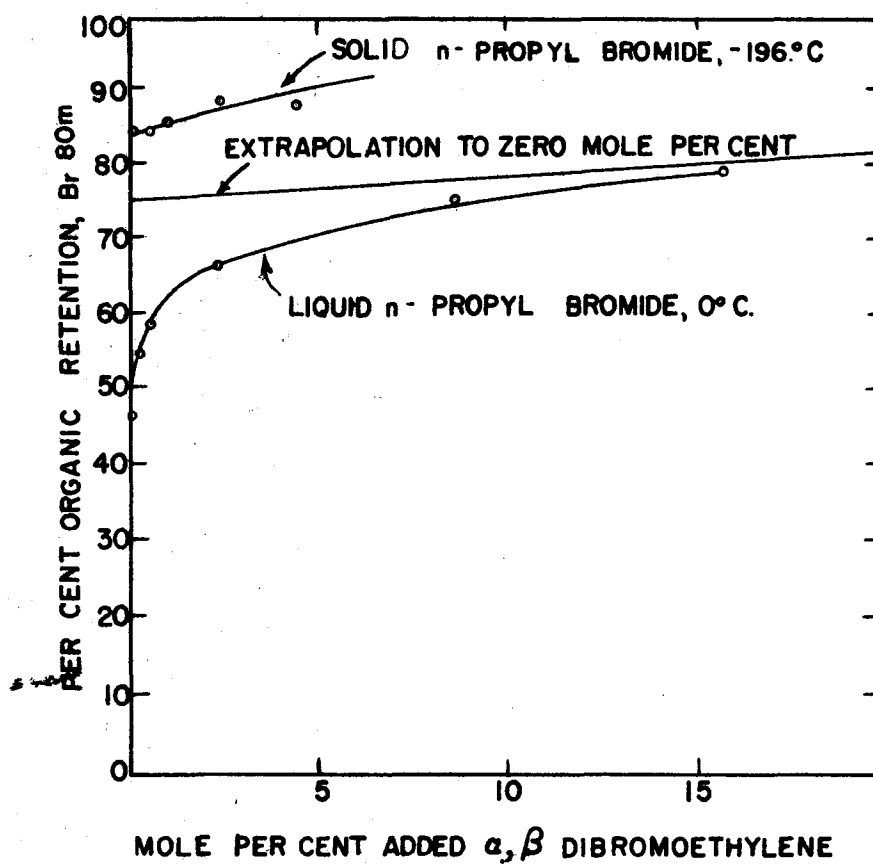


Figure 10. Retention of (γ, n) produced $\text{Br}^{80\text{m}}$ in n-propyl bromide as a function of α, β -dibromoethylene concentration at 0°C. and -196°C.

the initial sample (first ethyl plus methyl bromide) is 157 counts/min, the second ethyl plus methyl bromide sample is 29.8 counts/min and the third (ethyl bromide) is 43. Since the first two samples were diluted before counting, a correction factor must be applied as follows, $157 \times (8.0/5.0) = 251$ for the first sample and $29.8 \times (8.0/3.9) = 61$ for the second.

A curve of counting rate versus volume of distillate taken over was plotted for the three counting rates above. The curve leveled off to an estimated 39 counts/min for ethyl bromide. By noting the area under the curve above 39 counts/min it was found that approximately 99% of the methyl bromide activity came over in the first 5 ml of ethyl bromide distillate. The corrected counting rate for this sample is 251 counts/min. Subtracting 39 counts/min one arrives at the value of 212 counts/min, which is attributed to methyl bromide.

It was necessary to correct the 5 ml volume to the original volume in which the methyl bromide was dispersed prior to distillation. Since 13.4 ml of extracted n-propyl bromide were added to the mixture of carrier compounds in the still pot, it is evident that 90% of the methyl bromide that was originally dispersed in a volume of 13.4 ml has been concentrated into a volume of 5.0 ml, and the counting rate will have gone up accordingly.

The calculation in Table 3 for methyl bromide contains the above correction factors as well as the correction for the density of the ethyl bromide medium.

A similar estimate was made for the ethylidene bromide by subtracting counting rates for methylene and ethylene bromides from the peak counting rates of intermediate samples.

In the case of higher boiling or "polymer" activity above the trimethylene bromide, it was necessary to count a pure sample of trimethylene

Table 3

Sample calculation of percentage yields
for curves shown in Figure 2

Compound	Application of Correction Factors	% Yield
Methyl bromide	$\frac{212}{0.905} \times \frac{5.0}{13.4} \times \frac{1.00}{0.97} = 90.3$	1.2%
Ethyl bromide	$39 \times \frac{20.0}{13.4} \times \frac{1.00}{0.97} = 60$	0.8%
iso-Propyl bromide	$45.6 \times \frac{20.0}{13.4} \times \frac{1.00}{1.01} = 67.5$	0.9%
n-Propyl bromide	$458 \times \frac{20.0}{13.4} \times \frac{1.00}{1.00} = 684$	8.8%
Methylene bromide	$102 \times \frac{20.0}{13.4} \times \frac{1.00}{0.74} = 206$	2.7%
Ethylidene bromide	$27 \times \frac{3.4}{13.4} \times \frac{1.00}{0.74} = 9$	0.2%
Ethylene bromide	$79 \times \frac{20.0}{13.4} \times \frac{1.00}{0.74} = 159$	2.1%
Propylene bromide	$120 \times \frac{30.0}{13.4} \times \frac{1.00}{0.875} = 307$	4.0%
Trimethylene bromide	$127 \times \frac{20.0}{13.4} \times \frac{1.00}{0.865} = 220$	2.8%
"Polymers"	$513 \times \frac{8.0}{13.4} \times \frac{1.00}{0.865} = 352$	4.6%
Aqueous		$\frac{72.4\%}{100.5\%}$

bromide and then subtract its counting rate from that of the liquid remaining in the still pot. Since the counting rate for the final sample was 640 counts/min and that of the trimethylene bromide was 127 counts/min, the rate caused by "polymers" is about 513 counts/min. The total volume remaining in the still pot was 8 ml so that the "polymers" had been concentrated by a factor of $13.4/8$ in the distillation process.

All other yields were determined directly from the individual counting rates. All compounds for which carriers were added would disperse into the volume of each added to the still pot, so it is apparent that they would be diluted by factors of $13.4/20$ in all cases except propylene bromide which would be diluted $13.4/30$.

The sum of the corrected counting rates for the aqueous sample and the unfractionated n-propyl bromide was taken as 100%. The percentage total listed represents the sum of individual percentage yields plus the percentage yield of the aqueous sample. The curve for iso-propyl bromide is not shown on Figure 2 because it very nearly coincided with two others and would have made the graph difficult to interpret.

It is noted that the density factor of 0.74 for methylene bromide is used for ethylene bromide. In order to estimate the yield of ethylidene bromide it was necessary to correct the ethylene bromide counting rate to the value it would exhibit in a methylene bromide medium.

Recent evidence for a greater multiplicity of products (5) indicates that the very close agreement of the sum to 100% probably results partially from a cancellation of errors. However, all indications are that any further products would be present in very small amounts. No noticeable distillation peaks were observed other than the three here reported, and this is in agreement with the observations of previous workers (2). No attempt has been

made to determine the nature of the "polymer" activities, and there are undoubtedly a number of these higher boiling compounds produced.

The results of the (γ, n) studies compared to the previous (n, γ) studies (2) are reported in Tables 4 and 5. The (n, γ) results are for Br^{82} , but recent work by Levey and Willard (54) with Br^{80} indicates that the results for Br^{80} by neutron activation are very similar to those for Br^{82} . Thus, one might expect the yields for Br^{80m} from neutron capture to be essentially the same as those for Br^{82} .

From the very start little difficulty was encountered in obtaining reproducible retention values in the solid state irradiations. Such reproducibility gave encouragement at a time when liquid state irradiations were far from giving reproducible results. Previous workers (2) had indicated that impurities have little effect in the solid because they are, effectively, "frozen out".

The first solid run on n-propyl bromide listed in Table 4 represents the first successful separation of essentially pure fractions of all compounds which was attained. Because the various products were not all counted in the same tube, the results are not considered to be as accurate as those of the second run which is listed after it. The second run was one of the final runs made and should be quite accurate. But what is important is the close agreement of the two runs to themselves and to the previous (n, γ) work. Even more impressive is the agreement of the two runs in solid iso-propyl bromide and their similarity to the (n, γ) results for Br^{82} .

In the liquid irradiations the agreement between (n, γ) and (γ, n) reactions is not quite as striking. There seems to be a noticeable increase in yields of the dibromides, but very little change in the yields of the monobromides. There is some doubt as to the accuracy of the value for propylene bromide for

Table 4

Yields of products in n-propyl bromide

Reaction	Liquid State				Solid State		
	(γ ,n)	(n, γ) ^a	(γ ,n)	(n, γ) ^b	(γ ,n)	(γ ,n)	(n, γ) ^a
Mole % Br ₂	0	0	4.7	5	0	0	0
Temperature	30°C.	25°C.	0°C.	-	All at -196°C.		
Isotope	Br ^{80m}	Br ⁸²	Br ^{80m}	Br ⁸²	Br ^{80m}	Br ^{80m}	Br ⁸²
Compound	Percentage Yields						
Aqueous	46	65.3	72.4	76	11.3	10.9	11.6
Methyl bromide	1.4	-	1.2	1.4	2.0	0.8	-
Ethyl bromide	1.2	0.7	0.8	0.3	2.9	4.0	2.7
iso-Propyl bromide	1.9	1.7	0.9	0.8	3.8	3.4	3.4
n-Propyl bromide	19.7	17.1	8.8	8.6	32.3	28.7	26.9
Methylene bromide	4.0	1.8	2.7	1.1	2.3	3.2	2.4
Ethylidene bromide	-	-	0.2	-	-	0.5	-
Ethylene bromide	5.8	3.1	2.1	1.6	5.0	8.3	6.0
Propylene bromide	13.0	2.8	4.0	2.5	15.6	17.9	17.8
Trimethylene bromide	4.7	2.7	2.8	2.5	10.0	9.0	10.4
"Polymers"	<u>2.2</u> 99.4	1.5	<u>4.6</u> 100.5	4.9	<u>15.0</u> 100.2	<u>11.1</u> 97.8	12.1

^aFrom data of Libby and Fox (2).^bCalculated from data of Chien (4) as listed in a later reference (5).

Table 5

Yields of products in iso-propyl bromide

	Liquid State		Solid State			
Reaction	(γ ,n)	(n, γ) ^a	(γ ,n)	(γ ,n)	(n, γ) ^a	(γ ,n)
Mole % Br ₂	0	0	0	0	0	33
Temperature	0°C.	25°C.	All at -196°C.			
Isotope	Br ^{80m}	Br ⁸²	Br ^{80m}	Br ^{80m}	Br ⁸²	Br ^{80m}
Compound	Percentage Yields					
Aqueous	60.5	68.3	1.6	2.3	5.7	52
Methyl bromide	1.8	-	1.2	1.7	-	0.3
Ethyl bromide	0.6	0.7	2.4	2.6	1.7	0.3
iso-Propyl bromide	14.2	9.3	13.9	14.2	11.7	7.6
n-Propyl bromide	1.4	2.5	30.2	29.5	31.8	4.0
Methylene bromide	3.7	-	3.0	2.4	-	2.2
Ethylidene bromide	-	1.6	-	1.9	1.3	1.1
Ethylene bromide	2.6	5.4	6.5	6.8	4.5	2.9
Propylene bromide	8.5	2.3	20.4	17.3	18.5	14.2
Trimethylene bromide	0.9	0.8	6.6	8.3	7.5	3.5
"Polymers"	3.4	2.9	12.3	12.8	12.4	17.4
	<u>98.5</u>		<u>98.1</u>	<u>99.8</u>		<u>105.5</u>

^aFrom data of Libby and Fox (2).

the irradiation of liquid n-propyl bromide. The retention is about 7% higher than the value accurately determined by short runs. This particular sample of n-propyl bromide was not quite as highly purified as it might have been, and impurities or slight radiation damage could explain the increase. Hydrogen bromide is one of the primary forms of inorganic products, and it is possible that in a long irradiation the HBr activity would concentrate in the vapor above the irradiated liquid. Since no attempt was made to capture the vapors in the extraction process, it is conceivable that some inorganic yield could be lost in this way for long irradiations. Such a loss would give rise to a high value for retention.

If the above increase was spread throughout all compounds it would not affect their values much, but if it all went to the formation of one compound, such as propylene bromide, then this value would be quite high. Further runs should be carried out to obtain a better value for retention. It is suggested that a very small amount of bromine be present during irradiation to overcome any radiation damage effects.

The retention value for the run on liquid n-propyl bromide at 0°C. with 4.7 mole % added bromine is within one per cent of the value expected from the curve in Figure 8. A decrease in all yields except "polymers" is noted. The most impressive aspect of these results is their very close similarity to the data of Chien (4) for the (n,γ) reaction with 5 mole % added Br₂.

The retention value of 48% for the irradiation of solid iso-propyl bromide at -196°C. containing 33 mole % Br₂ falls on the curve shown in Figure 9. The most striking change noted as a result of added Br₂ is the drop of n-propyl bromide yield from 31.8% to 4.0%. One notes also an increase in "polymer" yield and only a slight decrease in propylene bromide

yield. The irradiation time for this run was cut short and as a result not as much activity was produced as is desirable. The total yield value of 105.5% for this run is partially explained by the low statistical accuracy due to counting rates.

Possible Isotope Effects

Parent Compound Yield Compared to Total Organic Yield

The theory that recoil atoms re-enter combination to produce the parent compound primarily by elastic collision mechanisms has been proposed by Libby (2,3,84). To test this theory it was desirable to check the n-propyl bromide yield compared to the total organic yield for $\text{Br}^{80\text{m}}$ and Br^{76} . As will be shown later in the discussion of results, if an elastic collision mechanism is important, one might expect a lower yield of the parent compound for Br^{76} than for $\text{Br}^{80\text{m}}$ because of the smaller mass of Br^{76} .

Liquid n-propyl bromide at 0°C . was irradiated for five hours at a beam intensity of about 400 roentgens per minute. The irradiated sample was extracted with the aqueous sulfite solution. Following the extraction a portion of the extracted n-propyl bromide was saved and counted. The remainder of the extracted n-propyl bromide was added to the mixture of carriers and fractionated. The n-propyl bromide fraction was counted for several days and its decay compared to that for the unfractionated n-propyl bromide sample. Figure 11 shows the parallel nature of the two curves. The expected decrease of parent compound yield for Br^{76} compared to $\text{Br}^{80\text{m}}$ is definitely not apparent. Actually, according to the ratios listed in Figure 11, the parent compound seems to show a very slight increase relative to the total yield. This increase, however, is within the statistical error of the counting rate of the parent compound sample.

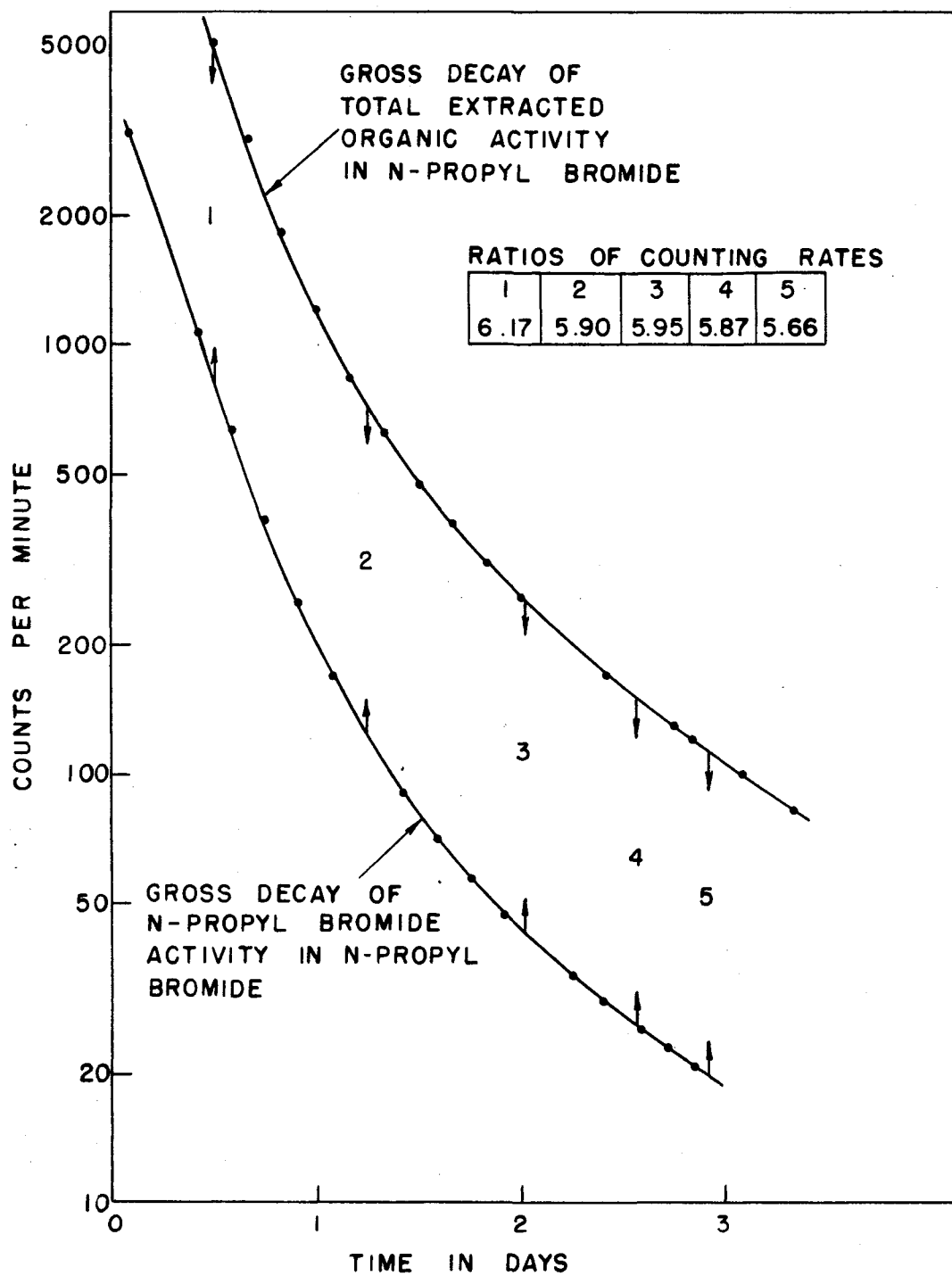


Figure 11. Curves showing the absence of a decrease in ratio of parent compound yield to total organic yield in going from 4.6 hour $\text{Br}^{80\text{m}}$ decay into 17 hour Br^{76} decay.

Since both samples contained essentially the same medium, density effects could not have entered in. Because of the very high energy of the particles emitted on decay any slight differences in wall thickness for the two counting tubes used should not have any significant effect. The glass wall thicknesses for all counting tubes are listed by the manufacturer as 30 mg/cm².

Retention of Br⁷⁶, Br⁷⁷, and Br^{80m}

One of the main reasons for attempting the analysis of the gross decay curve was to observe possible isotope effects on retention.

The curves of Figures 4 and 5 can be used to determine retentions for Br⁷⁶, Br⁷⁷ and Br^{80m} in solid n-propyl bromide at -196°C. Since the curve of Figure 4 represents the total retention or organic yield and the curve of Figure 5 represents the total yield, both organic and inorganic, the analysis of each curve into the three bromine activities makes possible a direct determination of retention for each bromine isotope. One needs only to correct the counting rates in one counting tube to what they would be in the other tube.

A given sample of n-propyl bromide containing Br^{80m} was divided into two portions. One portion was counted in the tube used above for the total yield, and the other was counted in the tube used for organic yield. The former tube gave a counting rate which was 0.87 of that in the second tube.

If one desires to use the aforementioned curves to calculate retentions, the counting rates found in Figure 4 must be multiplied by a factor of 0.87. The retentions for Br^{80m}, Br⁷⁶ and Br⁷⁷ as calculated from the curves were 87%, 67% and 62%, respectively. Since these are the results of only one run, it is definitely felt that they should be checked by future investigators.

Both of the above samples contained activities in forms of varying volatility, so it was felt absolutely necessary to quickly place both samples in given counting tubes and keep the tubes well stoppered during the progress of the counting. The nature of the decay curves in both cases indicates that no activity was lost due to boiling off of highly volatile components.

The very fact that different counting tubes were used raises the possibility of error. Thus if the glass wall were thicker in one tube than in the other the counting rate of one of the activities might be affected more than another because of the different energies of their emitted particles.

The $\text{Br}^{80\text{m}}$ was counted by means of the 2.0 Mev beta which is emitted by its immediate daughter, Br^{80} . The Br^{76} , on the other hand, was counted directly by means of its 3.6 Mev positron. The only radiation detectable in the decay of Br^{77} is the 0.34 Mev positron which is emitted in 5% of the decays. The half-thicknesses for a 2.0 Mev beta and a 3.6 Mev positron are 102 and 340 mg Al/cm², respectively, while the value for a 0.34 Mev positron is only 8 mg Al/cm². The first two half-thicknesses are large enough to indicate that slight differences in the thickness of the walls should be unimportant, but the very low value of 8 mg Al/cm² for the third is indicative of a high susceptibility to such differences.

The above difficulties are not at all insurmountable. One could easily check the relative counting efficiencies of two tubes for all three activities by placing a portion of the same sample in each tube and following the decay. Subsequent analysis would give counting rates for each activity in each tube. The rates could then be compared to give counting efficiency ratios for all

three activities. Thus, instead of the one factor of 0.87 as was used above, there might be three factors, one for $\text{Br}^{80\text{m}}$, one for Br^{77} and one for Br^{76} .

In a run on liquid iso-propyl bromide at 0°C . which was carried out prior to the above run the analysis of the decay curves for the total retained activity and for the total extracted activity indicated only a slight difference in yields for Br^{76} and $\text{Br}^{80\text{m}}$. The retention of Br^{76} seemed to be about 3 or 4% lower than that of $\text{Br}^{80\text{m}}$. However, since the densities of the propyl bromide and aqueous media were different, the results are probably not as accurate as the results for the above run on solid n-propyl bromide in which both samples were counted as liquid n-propyl bromide.

DISCUSSION OF RESULTS

Nuclear Reactions

The $\text{Br}^{79}(\gamma, 2n)\text{Br}^{77}$ and $\text{Br}^{79}(\gamma, 3n)\text{Br}^{76}$ reactions here reported have not previously been reported in the literature.

Since the main concern of this research was not with the complete proof of existence of the above reactions, only a few aspects of such proof were considered. The half-lives of the products as determined here agree quite closely with previously reported literature values. One run on a scintillation spectrometer gave energy lines of approximately the correct values for Br^{77} . However, not enough Br^{76} was produced to give observable lines.

Another indication of the production of these two nuclides was the relative zero time counting rates for Br^{76} and Br^{77} in the G.M. tubes. On a theoretical basis a much greater amount of the $(\gamma, 2n)$ produced Br^{77} would be expected than of the $(\gamma, 3n)$ produced Br^{76} . However, only 5% of the Br^{77} decays are by emission of a 0.34 Mev positron, the remainder being by electron capture, while Br^{76} decays almost entirely by emission of a 3.6 Mev positron. Since the 0.34 Mev positron has a half thickness of only 8 mg Al/cm², only a very small portion of these positrons would pass through the 30 mg/cm² glass wall of the counting tube. The 3.6 Mev positron on the other hand has a half thickness of 340 mg Al/cm² and would be only very slightly absorbed in the tube wall. The liquid medium would, of course, exhibit the same effect as the tube wall in decreasing the counting rate of the Br^{77} with respect to the Br^{76} . A correction factor for absorption coupled with the factor of twenty for the fraction of Br^{77} decays which are observable should

give a corrected zero-time ratio for the two counting rates which is approximately the same as the ratio of counting rates expected theoretically.

The $\text{Br}^{81}(\gamma, \alpha n)\text{As}^{76}$ and $\text{Br}^{79}(\gamma, \alpha n)\text{As}^{74}$ reactions had previously been reported in the literature (101), and it is evident that they were produced here. A short-lived activity, presumably 90 minute As^{78} , was also noted, but no attempt was made to determine its half-life. The above workers (101) had also reported the possibility of the $\text{Br}^{81}(\gamma, \alpha)\text{As}^{77}$ reaction. The As^{77} has a reported half-life of 39 hours. No such activity is apparent in the curve of Figure 3. (See page 49.)

Momentum Considerations and Isotope Effects

Libby (2,3,75,84) has proposed that recoil atoms re-enter combination as parent compounds primarily by an elastic collision mechanism. Thus, a high energy recoil atom making a direct collision with an atom of similar mass can transfer nearly all of its energy to the struck atom. It would then be captured by the remaining molecular fragment.

To test this hypothesis the experiment discussed on pages 70-72 was made to see if the ratio of parent compound yield to total organic yield would be different for Br^{80m} and Br^{76} . As is noted in Figure 11 no appreciable difference was evident although one might expect at least some change if an elastic collision mechanism is important.

The following equation gives the minimum energy that a particle can have following a direct collision with another particle,

$$E_r = E_1(M - M')^2 / (M + M')^2,$$

in which E_1 is the energy before collision, and M and M' are the masses of the two particles involved in the collision. Thus if a Br^{80} atom strikes

either a Br^{79} or a Br^{81} atom it can end up with a minimum energy of about $1/250,000$ th of what it had prior to the collision. But, if a Br^{76} atom hits a Br^{79} atom the minimum energy it can have is approximately $1/27,000$ th of its previous energy. For a Br^{76} atom striking a Br^{81} atom the factor is about $1/1000$.

Initial recoil energies from (γ, n) activation would be in the range of 100 to 500 kev. Assuming an initial recoil energy of 100 kev, which is approximately 4000 times the C-Br bond energy, it would be possible for a Br^{80} atom to end up with an energy of about one-sixth of the energy of the C-Br bond after a single collision. Using the same equation it is found that for a Br^{76} atom striking a Br^{81} atom the minimum energy would be 4 times the C-Br bond energy. According to Libby (75) the Br^{80} atom would be expected to be captured and form the parent compound. On the other hand, the Br^{76} would recoil with such force that it could not be captured.

Since the energy required to break the reaction "cage" is about 25% of the bond energy, a Br^{76} atom having an energy greater than 6000 ev could not lose enough energy in one collision with a Br^{81} atom to be recaptured by the parent fragment. It is evident that there is quite a large energy range in which a Br^{80} could be recaptured, whereas a Br^{76} atom could not. At lower energies glancing collisions could still result in non-capture.

An expression for average energy loss per collision has been developed (75). According to this expression the average energy loss for Br^{80} atoms striking Br^{81} atoms is very nearly the same as for Br^{76} atoms striking Br^{81} atoms. Thus, the average number of collisions required to lower either Br^{76} or Br^{80} to thermal energies is about the same. The significance of this is mainly in the fact that only when the atoms collide very nearly head-on will Br^{76} and Br^{80} atoms of a given energy end up with appreciably

different energies. And yet, the only collisions which can result in almost complete loss of energy are the very nearly head-on ones. For any case in which the energy retained after collision is less than about ten per cent of the energy held prior to collision the mass difference effect would be significant. Until the energy of the recoil atom is lowered to about 10 ev, there will be an expected effect due to mass differences. When the recoil atom has an energy of more than about 10 ev a glancing collision which leaves it with more than 10% of its original energy will allow it to escape from the reaction "cage". (The energy necessary to escape such cages is about 1 ev.) However, when the recoil atom reaches energies of 10 ev or less it can lose energy in inelastic collisions with whole molecules to form products other than the parent compound. If an elastic collision mechanism to produce the parent compound is important, all these considerations point to a lower ratio of parent compound yield to total organic yield for Br^{76} than for $\text{Br}^{80\text{m}}$. The fact that such a decrease is not apparent indicates that only a very small portion of the reactions involve "hot" atoms with energies greater than about 10 ev.

Other comparative data tend to discredit the fact that parent compounds are produced primarily by elastic collision mechanisms.

Referring to Table 4 (See page 67.) one notes only a very slightly larger n-propyl bromide yield for the (γ, n) reaction than for the (n, γ) reaction. One might expect a much larger value for the parent compound yield from the (γ, n) reaction, because of the much greater chance of an elastic collision mechanism taking place. But what is even more important is the fact that thermal reactions seem to be responsible for about half of the parent compound yield in n-propyl bromide. Referring to Table 4 on page 67 it can be seen that the presence of 5 mole % Br_2 lowers the

n-propyl bromide yield from 19.7% to 8.8%. As was previously mentioned (pages 56-58), most of this difference is considered to be the percentage yield due to thermal processes.

The fact that nonthermal reactions are practically independent of initial recoil energy is shown by the agreement of the n-propyl bromide yields for both (γ ,n) and (n, γ) reactions in liquid n-propyl bromide containing about 5 mole % added Br₂. If one assumes an average initial recoil energy of about 100 ev for the (n, γ) reaction, the values of 8.8% for (γ ,n) and 8.6% for (n, γ) indicate that recoil atoms above 100 ev energy rarely re-enter the parent compound as the result of one elastic collision.

The fact that the non-thermal organic yield for the (γ ,n) reaction in n-propyl bromide of 25% is only 4% higher than the 21% for the (n, γ) reaction, also indicates a lack of importance of elastic collision mechanisms.

Very recent work by Levey and Willard (54) has compared the effects of the Br⁷⁹(n, γ)Br⁸⁰ and Br^{80m}(I.T.)Br⁸⁰ reactions in the propyl bromides. Some of their data are compared with the results of the Br⁸¹(γ ,n)Br^{80m} reaction in scavenged n-propyl bromide as shown in Table 6. Again it is seen that even in the case of the isomeric transition activation a yield of 7.7% for n-propyl bromide is noted. These results seem to further agree with the postulate that elastic collision mechanisms to produce the parent compound do not often occur. Indeed in the case of the isomeric transition reaction the Br⁸⁰ atom would never have enough energy to be involved in an elastic collision of the kind that have been discussed above.

Results which have thus far been reported concerning retention in crystalline propyl bromides indicate the existence of an isotope effect. Libby and coworkers (2,84) have proposed a theory that initial recoil energy is important to the amount of retention because it determines the size of

Table 6

Comparison of product yields for the $\text{Br}^{80\text{m}}(\text{I.T.})\text{Br}^{80}$, $\text{Br}^{79}(\text{n},\gamma)\text{Br}^{80}$
and $\text{Br}^{81}(\gamma,\text{n})\text{Br}^{80\text{m}}$ reactions in liquid propyl bromides

Compound Irradiated	iso-Propyl Bromide			n-Propyl Bromide		
Mole % Added Br ₂	0	0	0	5	5	4.7
Mode of Activation	(n,γ) ^a (I.T.) ^β (γ,n)			(n,γ) ^β (I.T.) ^a (γ,n)		
Compound	Percentage Yield					
Ethyl Bromide	0.14		0.6	0.30	0.53	0.8
iso-Propyl Bromide	10.1	9.9 ^b	14.2	0.73	0.78	0.9
n-Propyl Bromide	1.0	2.9 ^b	1.4	7.7	7.7 ^c	8.8
Methylene Bromide			3.7	0.95	1.9	2.7
Propylene Bromide			8.5	2.29	4.7	4.0
Total Retention	23.6	21.4 ^b	36.0	21.0	20.8 ^c	27.6

^aFrom data of Levey and Willard (54).

^bAverage of three listed values (54).

^cAverage of four listed values (54).

the pseudo-liquid volume produced in the solid. In light of the preceding discussion such an explanation appears to rest on a weak foundation, and as will now be shown other data of the present research tend to discredit this theory.

Table 7 shows a comparison of the retention yields for various nuclear reactions in the crystalline propyl bromides. One notes an increase of 7% in n-propyl bromide and 13% in isopropyl bromide for the retention from the

Table 7

Retention in crystalline propyl bromides for $\text{Br}^{79}(\text{n},\gamma)\text{Br}^{80\text{m}}$,
 $\text{Br}^{81}(\text{n},\gamma)\text{Br}^{82}$ and $\text{Br}^{81}(\gamma,\text{n})\text{Br}^{80\text{m}}$ reactions at -196°C .

Compound	Nuclear Reaction	% Retention
n-Propyl Bromide	$\text{Br}^{81}(\text{n},\gamma)\text{Br}^{82}$	86.7 ^a
	$\text{Br}^{79}(\text{n},\gamma)\text{Br}^{80\text{m}}$	78.2 ^a
	$\text{Br}^{81}(\gamma,\text{n})\text{Br}^{80\text{m}}$	85
iso-Propyl Bromide	$\text{Br}^{81}(\text{n},\gamma)\text{Br}^{82}$	93 ^a
	$\text{Br}^{79}(\text{n},\gamma)\text{Br}^{80\text{m}}$	83 ^a
	$\text{Br}^{81}(\gamma,\text{n})\text{Br}^{80\text{m}}$	96

^aFrom data of Rowland and Libby (84).

(n,γ) produced $\text{Br}^{80\text{m}}$. These increases are in direct opposition to the recoil energy theory which proposes a decrease of retention in the solid when the initial recoil energy increases. Admittedly, the pseudo-liquid volume formed by the (γ,n) reaction would probably contain a higher density of radicals and a higher organic retention would result. But the size of the pseudo-liquid volume would be very much greater in the case of the (γ,n) reaction. Would the recoil atom ever reach the semi-molten volume proposed by Libby and Fox (2) before either entering organic or inorganic combination?

It is interesting to note that the retention values listed in Table 7 for $\text{Br}^{80\text{m}}$ by (γ,n) are in both cases quite close to those for Br^{82} by (n,γ) activation.

If Br^{77} is not included because of the inaccuracies discussed previously there remain the retention values of 87% for $\text{Br}^{80\text{m}}$ and 67% for Br^{76} .

This difference is in direct opposition to the recoil energy hypothesis. The average initial recoil energy following a $(\gamma, 3n)$ reaction would be expected to be less than that following a (γ, n) reaction unless all three neutrons were given off simultaneously in nearly the same direction.

If this lowering of retention for Br^{76} had been noted in the case of the liquid irradiation too, then one might suspect the mass difference mechanism suggested at the first of this section. However, since the momentum considerations failed to hold in other cases in which they might much more logically be expected to do so, one should be hesitant to postulate such a mechanism even if more accurate future data for the liquid propyl bromides indicate an isotope effect.

Increased retention yields in solid state irradiations for photo-induced reactions can be partially explained on an organic radical density basis, but decreased yields compared to those for (n, γ) activation do not seem to fit the picture. The fact that the retention for Br^{76} in solid n-propyl bromide is apparently less than that for any bromine isotope which has been produced by neutron activation indicates that other factors not yet understood must be taken into consideration.

Such isotope effect considerations are obviously in a state of confusion at present. Much more data are needed to clear up the picture. The fact that isotope effects have not been noted in alkyl iodides does seem to indicate that any variations in the alkyl bromides are primarily due to chemical causes or the delayed emission of γ 's.

In the (γ, n) reaction to form Br^{80m} it is conceivable that γ -rays are given off along with the neutron in producing the relatively stable Br^{80m} atom. If some of these γ 's are delayed long enough, the recoil atom might already have settled back into combination before the γ -ray were emitted.

If the γ -ray were of the proper energy, it could be internally converted and result in disruption of the newly produced molecule. This process might then be repeated by the emission of further such γ 's. It is conceivable that different isotopes or the same isotope by different modes of activation would have different emission properties. Such variations could be the cause for isotope effects.

Some Important Chemical Effects of the $\text{Br}^{81}(\gamma, n)\text{Br}^{80m}$ Reaction and Their Comparison to Those of Other Modes of Activation

Phase Effect Comparisons

As is apparent from Figure 6 (See page 54.), the phase effect which has been reported by other workers (2,84) for (n, γ) activation was also noted for the $\text{Br}^{81}(\gamma, n)\text{Br}^{80m}$ reaction in the propyl bromides. The fact that the results are quite similar for both nuclear reactions indicates that the determining factors for product yields are primarily chemical in nature.

The postulate of Libby and Fox (2) was that the increased retention in solid state irradiations is the result of dense fragmentation in a semi-molten volume at the edge of the pseudo-liquid volume and the increased energy necessary for a recoil atom to break out of the so-called reaction "cage". It was postulated that the recoiling atom had such a low energy when entering the semi-molten volume that in inelastic collisions with whole molecules, it would replace carbon and hydrogen atoms to form products other than parent compounds.

As Willard (6) has pointed out, Libby and Fox did not consider the possibility that inorganic reactions also occur with recoil atoms by non-

thermal processes. In other words, what is there about the solid phase irradiation which results in such a large increase in retention, when the semi-molten volume would be expected to have an increased number of inorganic as well as organic radicals? For one thing, in the more rigid solid phase the breakage of more C-C bonds would be expected, and this would result in an increased number of organic radicals without increasing the number of inorganic radicals. Another possibility is that suggested by Levey and Willard (54) concerning the effect of density in gas phase studies. They postulated that at higher densities the inorganic radicals might diffuse proportionately faster than the organic radicals. Certainly, in a semi-molten volume an organic radical would have much less freedom of movement than an H atom. (Inorganic radicals would be mostly H atoms although a small percentage would be Br atoms.)

The yield of trimethylene bromide in liquid iso-propyl bromide is very small. This is expected since trimethylene bromide has bromine atoms on the two end carbon atoms while iso-propyl bromide has its bromine atom on the center carbon atom. But in the solid phase the yield is increased over that in the liquid by a factor of 10. Such an increased yield can most logically be explained as a result of fragmentation into one and two carbon radicals which recombine to form the trimethylene bromide. In the liquid such radicals could more easily diffuse away from the site of their production than in the solid, and would have less chance of recombining.

One notes that no difference in yield of the parent compound is observed in liquid and solid X-ray irradiations of iso-propyl bromide. Thus, there seems to be little enhancement of this particular reaction which probably involves replacement of bromine atoms. However, it does appear here that a good deal of the iso-propyl bromide which might otherwise have been formed

isomerizes to give n-propyl bromide. This jump of n-propyl bromide yield from 1.4% in liquid iso-propyl bromide to 30% in solid iso-propyl bromide may have something to do with the orientation of molecules in the solid. This orientation may result in a greater number of excited propyl radicals, any one of which could capture the recoil bromine atom and isomerize to n-propyl bromide. The increase of n-propyl bromide yield in solid n-propyl bromide might also be explained by such an increased excitation of propyl radicals in the immediate "cage" around the recoil atom. Such excitation will be discussed further in connection with the relatively small yield of n-propyl bromide from solid iso-propyl bromide containing 33 mole % Br_2 .

As will shortly be discussed, the retention of $\text{Br}^{80\text{m}}$ in liquid n-propyl bromide for (γ, n) activation is about 13% higher than of $\text{Br}^{80\text{m}}$ for (n, γ) . This parallels the similar 7% difference in solid n-propyl bromide and the same effect is noted in iso-propyl bromide. It is certainly expected that the pseudo-liquid volume resulting from a (γ, n) produced $\text{Br}^{80\text{m}}$ atom would contain a much higher concentration of radicals than such a volume resulting from an (n, γ) produced $\text{Br}^{80\text{m}}$ atom. This suggests the possibility that the larger solid state retention noted for the (γ, n) reaction is the result of the greater proportion of reactions of recoil atoms with organic radicals in the pseudo-liquid volume. If the increase is taken care of in the pseudo-liquid volume then there will be no increase in the semi-molten volume.

A higher concentration of organic radicals has a much more noticeable effect in causing a higher thermal organic yield, than it does in increasing the nonthermal organic yield. Since thermal reactions would probably occur only to a small extent in a semi-molten volume, one might expect that both (n, γ) and (γ, n) produced $\text{Br}^{80\text{m}}$ would form about the same percentage of organic products in the semi-molten volume.

Relative Yield Comparisons

The fact that the relative yields for all organic compounds are so nearly the same for various modes of activation either for liquid or solid irradiations indicates that probability factors are important in determining yields. Only in the case of the iso-propyl bromide yield in liquid iso-propyl bromide is there an appreciable increase in parent compound yield for the (γ, n) compared to the (n, γ) reaction. In general, for reactions which should not be very dependent on radical density, the yields are nearly the same no matter what the mode of activation. Trimethylene bromide could hardly be produced as a result of a thermal diffusion reaction in iso-propyl bromide, and its yield is, as expected, very small for both the (γ, n) and (n, γ) reactions. There is, in other words, a certain small probability that the appropriate condensation of fragments or rearrangement of bromine atoms will occur to give trimethylene bromide no matter what the initial nuclear reaction is.

Contemporary workers (97,98) have indicated that various modes of activation in liquid alkyl iodides produced no appreciable differences in retention. Recently, however, it has been reported that the $\text{Br}^{79}(n, 2n)\text{Br}^{78}$ reaction in n-propyl bromide gives rise to a retention of 44% (102). The results of the present research give a value of 47.4% for the $\text{Br}^{81}(\gamma, n)\text{Br}^{80m}$ reaction. These values are both appreciably higher than the value of 34% previously reported for the (n, γ) formation of bromine activities.

As is evident from the results for scavengers the increased retention for the (γ, n) reaction is primarily due to thermal diffusion type reactions. This would seem to be expected on the basis that the main effect of increased recoil energies would be a greater production of radicals in the immediate

vicinity of the recoil atom. The breakage of C-C bonds could increase the number of organic radicals without increasing the number of inorganic radicals. However, such thermal reactions would usually involve organic radicals, because of the much faster diffusion of inorganic radicals which would cause their concentration to decrease more than that of the organic ones.

One important fact to note is that if one compares the various yields resulting from (n,γ) and (γ,n) reactions in liquid propyl bromides the most noticeable increases are in the production of one and two atom compounds, and propylene bromide. In the solid state irradiations only ethylene, methylene and ethyl bromides show appreciable increases for the (γ,n) compared to the (n,γ) reaction.

For nonthermal reactions as shown by the propyl bromides containing 5 mole % added Br_2 , the same increase in yields for ethyl, methylene, and ethylene bromides is noted, whereas only propylene bromide of all the others shows an appreciable increase.

Again the comparison of the I.T. (isomeric transition), (n,γ) and (γ,n) results shown in Table 6 indicates a higher yield for methylene bromide by (γ,n) than by either (n,γ) or I.T. reactions.

Such data indicate an increased number of one and two carbon radicals both in the reaction "cage" in which nonthermal reactions take place, and in the immediate vicinity outside of the "cage" in which thermal reactions occur.

The yield for propylene bromide is higher for both (γ,n) and (I.T.) reactions than for the (n,γ) reaction. This latter fact seems to indicate a higher degree of excitation of propyl radicals in the case of the (γ,n)

than in the (n, γ) case, because the I.T. reaction would almost certainly involve excitation of propyl radicals, even to the extent of forming ions, as a result of the high positive charge on Br atoms produced by the isomeric transition.

This greater excitation of propyl radicals seems to be indicated by the increased production of propylene bromide in the (γ ,n) reaction compared to the (n, γ) reaction. The fact that the n-propyl bromide yield rises so sharply in the solid state irradiation of iso-propyl bromide compared to the liquid irradiation gives credence to the idea of excited iso-propyl radicals which isomerize with a switch of bromine to an end carbon. Such increased excitation in the solid might be expected because of the more rigid structure of the solid compared to the liquid.

In the run on solid iso-propyl bromide with 33 mole % Br₂ added a yield of only 4.0% for n-propyl bromide was noted. This is very much less than the yield in pure solid iso-propyl bromide. The overall retention for such a bromine concentration is 48%, which is just half of that for no added Br₂. Thus one might expect all yields to be one half as great in the 33 mole % bromine mixture. However, the "polymer" yield actually shows an increase, and the propylene bromide shows only a slight decrease.

If only a dilution effect were noted the yield of n-propyl bromide would be about 16%, "polymers" about 6% and propylene bromide about 9%. The actual n-propyl bromide yield is 12% below the expected value, and the sum for propylene bromide and "polymers" is 16% above the expected value. It is evident that many of the reactions which would normally form n-propyl bromide ~~form~~ propylene bromide and other dibromo and tribromo compounds as a result of the large amount of bromine available. In the process of re-

acting with bromine atoms the highly excited propyl radicals apparently can add varying numbers of bromine atoms.

The term "polymer" is obviously not the most correct word to describe all high boiling products. Undoubtedly, some of these products are polybromo compounds of methane, ethane and propane which are definitely not polymeric.

Comparisons of the Scavenger Effects

The effect of scavengers in liquid propyl bromides parallels that noted by other workers for the (n,γ) reaction (82,84) and the $(n,2n)$ reaction (102).

Table 8 shows a breakdown of organic and inorganic yields into thermal and nonthermal reactions for three types of activation in the propyl bromides. Such a breakdown is based on the assumption that the reactions which are not affected by scavengers are nonthermal, and those which are affected are thermal.

In comparing the results of the (n,γ) activation with those of the (γ,n) activation in liquid n-propyl bromide one notes a much small percentage of nonthermal inorganic reactions and a much larger percentage of thermal organic reactions for (γ,n) activation. Only a slightly greater value is noted for the nonthermal organic reactions for (γ,n) activation. The percentages for thermal inorganic reactions are essentially the same.

Such a breakdown indicates a higher proportion of thermal reactions for the (γ,n) than for the (n,γ) activation method. The reason for the large decrease in nonthermal reactions is not too clear. Such a decrease would result partially from the increase in nonthermal organic yield because of the larger number of organic radicals expected in the "cage" wall for the (γ,n) reaction. Any further decrease indicates a greater ability of recoil

Table 8

Percentage yields of thermal and nonthermal reactions in
n-propyl bromide

Irradiation Conditions	Liquid		Solid at -196°C.
Mode of Activation	(n,γ) ^a	(γ,n)	(γ,n)
Type of Reaction	Percentage Yields		
Nonthermal Inorganic	40	25	12
Thermal Inorganic	26	28	3
Thermal Organic	13	22	29
Nonthermal Organic	21	25	56

^aFrom data of Roy, Hamill and Williams (82).

atoms to escape the "cage" wall and enter into thermal reactions. One must remember that it is not necessary for a Br atom to undergo any reaction to end up in an extractable form. Once a Br atom gets away from the initial high density of organic radicals, it will almost certainly be extracted as inorganic bromine whether inorganically combined or free.

The artificial breakdown of reactions in solid n-propyl bromide as shown in Table 8 is probably far from being exact, but does indicate the presence of at least some thermal diffusion reactions in the solid. In both propyl bromides the relatively sharp initial drop in retention with added Br₂ is indicative of some thermal reactions. Certainly if an atom escapes the reaction "cage" while still in the pseudo-liquid volume, it can diffuse some before resolidification takes place. As a result of such diffusion it may quickly collide with one of the great number of radicals

expected in the pseudo-liquid volume. One would expect very little diffusion and resultant thermal interaction once the medium had resolidified.

One aspect which was not considered above is the effect of bromine on the crystal structure of n-propyl bromide. Another, of course, is the fact that large amounts of bromine would increase the number of inorganic radicals at the expense of the organic radicals. These effects might be partially responsible for the nonlinearity noted in Figure 9. (See page 61.) If not all nonlinearity were due to scavenger action, the correct extrapolation to zero bromine concentration would result in a smaller value for thermal organic reactions than is listed in Table 8.

Some Miscellaneous Comparisons

One notable aspect of the data comparing the I.T., (n,γ) and (γ,n) reactions (See page 80.) is the yield of n-propyl bromide in liquid iso-propyl bromide. Yields of 1% and 1.4% are noted for the $\text{Br}^{79}(\text{n},\gamma)\text{Br}^{80}$ and $\text{Br}^{81}(\gamma,\text{n})\text{Br}^{80\text{m}}$ reactions, respectively, while the $\text{Br}^{80\text{m}}(\text{I.T.})\text{Br}^{80}$ reaction gives a yield of 2.7%. Since the Br^{80} from isomeric transition is highly charged, it would most likely react by means of an ionic mechanism. The higher yield for the I.T. reaction might indicate that an ionic mechanism for the production of n-propyl bromide from iso-propyl bromide is more highly favored than a radical mechanism.

The recent data of Evans and Willard (5) has indicated a greater multiplicity of products than had previously been reported. Actually, in looking at the chromatographic patterns reported by the above workers it appears that most of the new products have boiling points higher than trimethylene bromide, which is the highest boiling fraction separated in the present work.

It had been previously expected that several "polymer" compounds were produced, but no real attempt was made to determine their nature.

Since n-butyl bromide and n-amyl bromide have boiling points very nearly coincident with methylene and ethylene bromides, respectively, part of the yields attributed to these latter two compounds could be attributed to the longer chain compounds. Chien (4) has reported a yield of about 0.3% for n-hexyl bromide in liquid n-propyl bromide with 5 mole % added Br_2 . This is a small yield and indicates that other long chain bromides would contribute very little to the total retention yield.

Mechanism

Considering all the data here listed and other previous data, a qualitative picture of the mechanism as it is understood by the author is in order.

For the irradiation of a liquid propyl bromide with high energy γ -rays the following description of the recoil process might be postulated.

The nucleus of a Br^{81} atom is struck by a high energy γ -ray forming a highly excited compound nucleus. The compound nucleus loses a neutron to form a Br^{80*} nucleus which is still probably excited above its ground state level and therefore will emit some γ -rays in stabilizing as a relatively stable Br^{80m} atom.

If the neutron is not given off within about 10^{-14} seconds after the γ -ray hits the nucleus bond rupture will occur as a result of recoil from the γ -ray alone. The energy of recoil from such γ 's will be about 2 to 5 Kev. But as soon as the neutron is emitted the Br^{80m} atom will recoil with an energy of about 100 to 500 kev. There is no question, but that such energies will cause the recoil atom to break away from the parent molecule.

Such high energy bromine atoms will undoubtedly cause a great degree of fragmentation in the immediate vicinity of their paths. But even with such high initial energies the average atom only requires about ten elastic collisions with bromine atoms to reduce its energy to the thermal energy range.

As has been indicated by the present research and other investigations (54,102) very few high energy bromine atoms undergo direct elastic collisions to form parent compounds. Of these few such collisions some could give rise to inorganic products as well as organic products.

When the energy of the atom has decreased to about 10 ev it collides with whole molecules in inelastic collisions. About 50% of these recoil atoms collide in such a way that they do not have enough energy to escape the "cage" of highly excited molecules and radicals directly surrounding them. The nature of the various products formed in such a "cage" and their relative yields is most likely dependent on two main factors (1) the relative probabilities for the presence of various excited molecules or radicals in the reaction "cage" and (2) the ability of excited molecules or radicals to rearrange, split or polymerize into new chemical forms. According to the results of the present research nonthermal "cage" reactions account for about 50% of all reactions. Half of these nonthermal reactions result in inorganic combination and half, in organic combination.

About 50% of the recoil atoms escape the reaction "cage" and thermally diffuse into the medium. In the immediate vicinity of the reaction "cage" a high density of free radicals is concentrated, consisting of fragments which were formed as the result of the energy transfer processes initiated by the recoil atom.

The thermal atom may meet an organic or inorganic radical as it diffuses and thus enter into either organic or inorganic combination. Again the relative yields will depend on the relative probabilities for various radicals being formed. The fact that organic radicals will diffuse much more slowly than inorganic radicals, which are primarily H atoms, will result in a higher relative density of organic radicals with respect to inorganic ones. The diffusion rates would thus have something to do with the yields of products, a higher diffusion rate resulting in a lower yield.

The mechanism in the solid is complicated by the fact that a pseudo-liquid or even gaseous volume is produced around the path of the recoil atom. The orientation of molecules in the solid and the fact that they are more tenaciously held together than in the liquid would probably give rise to a much greater amount of fragmentation in this pseudo-liquid volume than in the ordinary liquid.

It is the postulate of this author that the more fragmentation that occurs, the higher will be the organic yield. This is based on two facts. (1) The breakage of C-C bonds increases the number of organic radicals without increasing the number of inorganic radicals. (2) Inorganic radicals will diffuse faster than organic radicals, resulting in a smaller concentration of inorganic radicals in the vicinity immediately outside the reaction "cage". On this increased fragmentation basis one would expect a higher proportion of thermal organic retention in the pseudo-liquid than in the ordinary liquid. The present results indicate some scavenging effect on thermal reactions in the solid state irradiations, and such an effect would almost necessarily occur in a liquid medium where diffusion could occur.

Any recoil atoms which were still uncombined upon reaching a semi-molten region would most likely enter organic combination because the organic radicals would be much less free to move than inorganic radicals, and, as was just mentioned the breaking of C-C bonds would give rise to organic radicals without producing inorganic radicals.

Finally as resolidification takes place, excitation of molecules might be transferred from one molecule to the next. Thus, a recoil atom resting next to a molecule excited by such an energy transfer process might enter into combination with the molecule and be retained as organic yield.

If the resulting structure were open enough a bromine atom might diffuse a little even in the solid, but this probably would not add appreciably to the retention.

Whatever the mechanism in the solid, one thing is certain in propyl bromides, the crystalline state definitely enhances the formation of organic products containing recoil atoms. This is something which has not been apparent for alkyl iodides.

In postulating the above mechanisms for the propyl bromides it is painfully evident that not enough data is yet available to give a completely general picture of what happens when a solid is irradiated. Why are the retentions so different for alkyl bromides and so nearly the same in the alkyl iodides? Perhaps no such general picture will be forthcoming. That is to say, that variations in chemical nature may necessitate considering each system as a special case.

The apparent differences of retention in the solid phase irradiation for various isotopes, have not been satisfactorily explained, and future investigators should find work along these lines particularly fruitful in

more completely explaining the mechanisms. Perhaps relative diffusion rates of the various isotopes are important in determining their retentions. Another aspect would be the importance of delayed γ 's on resulting chemical effects. Further data along these lines is much needed.

Finally, the practical aspects of synthesizing tagged organic compounds with recoil atoms is another phase of the field which should not be overlooked.

CONCLUSIONS

Five radionuclides have been observed in the present investigation. These are produced by the following nuclear reactions: $\text{Br}^{81}(\gamma, n)\text{Br}^{80m}$, $\text{Br}^{79}(\gamma, 2n)\text{Br}^{77}$, $\text{Br}^{79}(\gamma, 3n)\text{Br}^{76}$, $\text{Br}^{79}(\gamma, \alpha n)\text{As}^{74}$ and $\text{Br}^{81}(\gamma, \alpha n)\text{As}^{76}$. Gross curves were analyzed into the above component activities. The photo-nuclear reactions to produce Br^{77} and Br^{76} have not previously been reported in the literature. The reaction $\text{Br}^{81}(\gamma, \alpha)\text{As}^{77}$ which was previously reported was not here observed.

Four (γ, n) runs on liquid n-propyl bromide which had been extensively purified gave a Br^{80m} retention of $47.4 \pm 0.9\%$, compared to a Br^{80m} retention of 34% by (n, γ) activation. The (γ, n) value for iso-propyl bromide was 36% which is higher than the reported 30% (n, γ) retention value. The (γ, n) Br^{80m} retentions in solid n-propyl and iso-propyl bromides at -196°C . were found to be 85 and 96%, respectively, compared to the respective values of 78 and 83% previously reported for the (n, γ) Br^{80m} reaction. These solid state results are in opposition to the initial recoil energy hypothesis postulated by Libby and coworkers.

The scavenging effects of bromine and α, β -dibromoethylene which were noted in liquid n-propyl bromide for the $\text{Br}^{81}(\gamma, n)\text{Br}^{80m}$ mode of activation indicate a breakdown of reactions as follows: 25%, nonthermal organic; 22%, thermal organic; 28%, thermal inorganic; and 25%, nonthermal inorganic. The respective values for the (n, γ) reaction have been reported to be 22, 12, 26, and 40%.

Scavenger effects seem also to have occurred in crystalline propyl bromides at -196°C ., providing evidence that thermal reactions occur in the

pseudo-liquid volume which is produced in the solid around the recoil atom as it loses its energy to the solid medium.

Irradiated samples of the propyl bromides were fractionally distilled to determine the percentage yields of many of the organic products formed as a result of the photonuclear production of $\text{Br}^{80\text{m}}$. The yields in the solid state show a very striking similarity to those for the $\text{Br}^{81}(\text{n},\gamma)\text{Br}^{82}$ activation. In the liquid state there are noticeable increases in yields of compounds formed as the result of the breakage of C-C bonds and in the yield of propylene bromide. The yield of parent compound in liquid n-propyl bromide containing 4.7 mole % added Br_2 is only 8.8% compared to a yield of 19.8% in pure n-propyl bromide, which indicates that a large proportion of the parent compound is formed by thermal reactions. In the presence of Br_2 as a free radical scavenger very striking agreement was observed between (γ,n) and (n,γ) activation indicating among other things that the much greater energy of recoil atoms following the (γ,n) reaction does not increase the parent compound yield.

The ratio of parent compound yield to total organic yield in liquid n-propyl bromide was found to be very nearly the same for Br^{76} and $\text{Br}^{80\text{m}}$. Elastic collision mechanisms to produce the parent compound should result in a smaller ratio for Br^{76} than for $\text{Br}^{80\text{m}}$.

Analysis of decay curves resulting from γ -irradiation of solid n-propyl bromide at -196°C . into $\text{Br}^{80\text{m}}$, Br^{76} , and Br^{77} activities allowed the calculation of retention values which were, respectively, 87%, 67% and 62%. The large difference in the values for $\text{Br}^{80\text{m}}$ and Br^{76} indicates some isotope effect. The values, however, represent the results of only a single run and could be in error. The fact of importance here is that the curves can be analyzed, thus making such retention calculations possible. It is hoped

that future investigators will check these values.

The above results, in general, indicate some new ideas about the mechanism by which $\text{Br}^{80\text{m}}$ atoms re-enter combination. It appears that the initial recoil energy is unimportant in determining yields, except in the greater production of radicals. The random fragmentation theory of Willard seems to be favored by the very close similarity of percentage yields for the (γ, n) and (n, γ) modes of activation. To be more explicit one might say that the relative yields of organic products are based mainly on the probabilities for the random formation of each. Elastic collision mechanisms at energies above 10 ev to produce the parent compound are not important, and probably contribute to not more than about 3% of the total retention.

The greater production of radicals which occurs as a result of higher energy recoil atoms or as the result of a change of state from liquid to solid probably enhances retention for two main reasons. (1) Breakage of C-C bonds produces organic radicals but not inorganic ones; and (2) H atoms, which are the primary inorganic radicals, will diffuse away much faster than their organic counterparts. Both of these factors would increase the probability of a recoil atom being captured by an organic radical and thus increase the retention.

The reasons for isotope effects are not clear from the data which have thus far been obtained. The relative diffusion rates for the various isotopes may be important. Delayed γ 's resulting in bond rupture after a recoil atom has recombined may also explain retention differences for various isotopes. The investigations of these aspects of the field should prove quite useful in gaining a better understanding of the various mechanisms by which recoil atoms re-enter combination.

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